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DEVELOPMENT OF A PREPROTOTYPE HYPERFILTRATION

WASH WATER RECOVERY SUBSYSTEM

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

UNDER CONTRACT NAS 9-15183

BY

BIOTECHNOLOGY

ADVANCED SYSTEMS DIVISION

LOCKHEED MISSILES & SPACE COMPANY, INC.



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FINAL REPORT

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## SECTION 1

INTRODUCTION

Reclamation of waste water on board an extended mission spacecraft is probably the most important step in the regenerative life support cycle, because the weight savings are large compared to the system penalties associated with the process. Carbon dioxide reduction and oxygen generation techniques require relatively high power and more complicated equipment while recovering less usable material.

Long duration space missions will require development of wash water treatment methods that provide for water reuse (1, 2). Average hydraulic loading can amount to 1.3 cm<sup>3</sup>/s (30 gal/day), with a peak load of 3.5 cm<sup>3</sup>/s (80 gal/day) (3). Preferred treatment methods should operate at high water recovery levels to reduce the amount of makeup water required. The quality of water produced should be compatible with standards recommended by the National Academy of Science. The NAS standards require that the water be acceptable from a health and comfort standpoint based on chemical and microbial impurities.

In previous studies sponsored by NASA, a multi-filtration scheme consisting of filtration, carbon adsorption, and ion exchange has been explored (4-6). More recently, the use of hyperfiltration (also referred to as reverse osmosis or RO) has been investigated (7-9) since it has relatively low specific energy requirements (7). It has been demonstrated that certain hyperfiltration membranes offer a feasible means of purifying wash water to meet NASA specifications.

Two basic approaches have been taken in the utilization of hyperfiltration for wash water recovery. They differ in the method employed to control microbiological activity in the recycled water. The initial approach, which was studied extensively, involved the utilization of the DuPont hollow fiber permeator and the Westinghouse tubular module operating at ambient temperature (10). In this system, relatively large doses of biocide (up to 1 percent) were used to control microbial activity. Since biocides require a long contact time, may have adverse dermatological effects, and may interact with membrane material, a second approach was undertaken, that of operating at pasteurization temperature of 347 K (165 F).

Under a series of jointly sponsored S.W. and NASA/HDQS contracts, hyperfiltration membranes capable of operation at high temperatures have been developed and evaluated. Some of the membranes studied include: (a) sulfonated polyphenylene oxide (SPOO) (11), (b) polybenzimidazole (PBI) (12), (c) a cross-linked polyethylenimine - (PEI) tolylene 2,4 diisocyanate (TDI) membrane designated NS-100 (13), and (d) dynamically formed dual layers hydrous Zr (IV) oxide covered with polyacrylic acid (14) (Zro-PAA).

The application of dynamically formed membranes to spacecraft wash water purification has been under extensive study since 1972 by Clemson University (14) for NASA/JSC. In the studies to date, ZrO-PAA membranes have proven highly reliable during extended operation at actual wash water temperatures while displaying excellent, stable performance (i.e., permeate flux and solute retention). As a result of these tests, NASA/JSC has selected the ZrO-PAA membrane for incorporation into a preprototype system.

The program carried out to advance the development status of the ZrO-PAA membrane technology to preprototype hardware status is presented herein.

### 1.1 Background

Hyperfiltration is a pressure-driven separation process employing a semi-permeable membrane which selectively permeates water while rejecting suspended and dissolved species at the membrane surface. One mechanism by which rejection occurs has been termed the "solution-diffusion" mechanism, in which the permeability of the membrane to any constituent is proportional to the product of its solubility in the membrane and its diffusivity through the membrane. Since diffusivity is inversely proportional to the molecular size, the larger the molecular size of the solute in the feed, the higher the membrane rejection. In general, ionic species and large organics will be highly rejected by hyperfiltration, and small hydrogen-bonding organics and non-ionized acids and bases will be poorly rejected.

In order to design a hyperfiltration system to have minimum weight, volume, and power requirements, the effect of various operating parameters on system performance must be evaluated. The parameters, which define system performance, include membrane flux (capacity) and solute rejection efficiency. The operating conditions which affect system performance include:

- o Feed Pressure
- o Pressure drop across the module (fixes average feed pressure).
- o Feed Concentration
- o Conversion across the module (fixes average feed concentration).
- o Temperature
- o Feed velocity across the membrane surface.
- o Mode of system operation (i.e., continuous, one-through, batch, feed-and-bleed, etc.).

The dynamic membrane module represents the basic element in the hyperfiltration wash water recovery subsystem and received the greatest attention in the development program. Research on dynamic membranes began in 1965 at the Oak Ridge National Laboratory where it was first discovered that a precipitate of Ti (IV) oxide in a porous Sela's Flotronics silver filter formed a salt rejecting layer later termed a dynamic membrane. This discovery led to additional studies in which the potential of other metal oxides to form dynamic membranes was evaluated. Some of the metal oxides investigated included Zr(IV), Fe(III), Sn(IV), and U(VI). Zr(IV) received the most attention and, in subsequent studies, improved separation characteristics and membrane reproducibility were obtained by a dual layer forming procedure utilizing polyacrylic acid (PAA) as a second layer.

Relative to other polymeric membranes, dynamically formed membranes are characterized by high permeate fluxes, moderate solute rejection levels, and decreased solute rejection in the presence of polyvalent anions and with an increase in solute concentration. Owing to their unique properties, dynamic membranes are best suited for the treatment of water solutions containing relatively low concentrations of monovalent solutes, such as would be found in spacecraft wash water.

The application of ZrO-PAA membranes for wash water treatment has been studied extensively by Clemson University under a contract (15) from NASA/JSC. In their studies, short-term effects of pressure, temperature, and feed velocity and membrane performance were determined over a wide range of operating parameters. The effects of system pressure and operating temperature were found to be within the general trends predicted by theory, i.e., increased permeate flux with increasing pressure and temperature and increased solute rejection with increasing pressure. The influence of feed velocity on both membrane flux and solute rejection in short-term tests was minor in the investigated range of 1.5 to 7.7 m/sec.

In a subsequent study (16), a 90-day life test was undertaken and focused on long-term effects of feed velocity on membrane performance. During these tests, feed velocities as low as 0.16 m/sec were investigated. Performance at such velocity levels are of special interest for the design of both the hyperfiltration system and module because they are in the range of once-through operation. The tests indicated that, in spite of the low velocities employed, acceptable performance characteristics were realized. Product water flux levels between 5 and 50  $\mu\text{m}^3/\text{m}^2\text{-sec}$  (10-100 gpd/ft<sup>2</sup>) were observed. The measured solute rejection and calculated values for rejection, in a once-through module operating at 90 percent conversion, are summarized in Table 1-1.

The procedure employed at Clemson University for the formation of dynamic membranes is given in Table 1-2. The chemicals used in forming the first layer of the membrane include zirconyl nitrate and sodium nitrate. A pH of 2 is required in the membrane formation. Two types of polyacrylic acid (Rohm and HAAS Aerosyl A-1 and A-3) have been used to form the membrane. Although data indicate that both types of PAA result in a similar membrane, future work may show that one is to be preferred.

Cleanliness of the system has been shown to be essential during membrane formation and requires the use of high purity chemicals and distilled water. The system must be thoroughly cleaned in accordance with the instructions of Table 1-2 before membrane formation is attempted.

In addition to cleanliness, membrane formation is sensitive to formation pressure and feed velocity. Clemson personnel (17) strongly recommend that the membrane be formed at final operating pressure and at a linear velocity of 3 to 10 m/sec.

Membrane regeneration can be exercised when membrane performance has declined or when unacceptable membrane performance is obtained after membrane formation.

TABLE 1-1

APPROXIMATE REJECTIONS OBTAINED IN THE  
90-DAY LIFE TEST (AFTER REFERENCE (18))

<u>COMPONENT</u>	<u>INITIAL</u> <sup>(1)</sup>		<u>FINAL</u>	
	<u>INTRINSIC</u>	<u>SYSTEM</u>	<u>INTRINSIC</u>	<u>SYSTEM</u>
CONDUCTIVITY	88%	73%	80%	60%
TOC	90%	77%	80%	60%
AMMONIA <sup>(2)</sup>	85%	68%	75%	51%
UREA	60%	33%	50%	24%

(1) BASED ON A MODULE PRECONDITIONED WITH WASH WATER FOR 300 HOURS

(2) ESTIMATED VALUES



TABLE 1-2

MEMBRANE FORMATION PROCEDURE

SYSTEM CLEANING: Hot phosphate wash (optional), drain and rinse.

1 Molar nitric acid wash for one hour at 50°C. Drain and rinse.

1 Molar sodium hydroxide wash for one hour, cold.

Repeat acid and base wash if bubbles occur. Drain and rinse.

During cleaning, all passages must be subjected to circulation of fluid. Stainless steel tubes must be cleaned in nitric acid prior to formation; ceramic tubes require no cleaning.

Formation of Zirconium Layer:

Fill with distilled water or equivalent. Add 0.04 - 0.05 molar  $\text{NaNO}_3$  and 0.04 g/l  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ . Circulate the solution at 20-45°C past the membrane support tube at 5 to 10 meters per second, raising the pressure to  $6.5 \times 10^6 \text{ N/m}^2$  as soon as practical. A flux decrease to  $2 \times 10^{-4} \text{ m/sec}$  or below indicates the membrane has formed.

Formation of PAA Layer

Add acid to lower the pH to 2.0 using  $\text{HNO}_3$ . Add 50 ppm PAA (Rohm and Haas Acrysol, 25% solution, A-1 or A-3). In  $\frac{1}{2}$  hour increments, raise the pH in units (2 to 3, 3 to 4, etc.) to pH 7 or 8 using NaOH. The acid excursion may be repeated for some improvement in performance.

Regeneration

Regeneration consists of a low pH excursion with salt ( $\text{NaCl}$  or  $\text{NaNO}_3$ ) and PAA as the constituents. The PAA amount may be less than 50 ppm or even zero. The process is beneficial in restoring performance sometimes lost during storage.

The regeneration procedure basically entails a PAA retreatment. When membrane performance degrades and regeneration is no longer effective in restoring acceptable membrane properties, the dual layer coatings can be removed from the porous support and a new membrane cast. The procedure for restoring the ceramic supports is to fire them in an air atmosphere at 973K (1292 F) for 2 to 3 hr; stainless steel supports are fired at 530 K (500 F).

### 1.2 Program Objective

The objective of this program is to design, develop, and test a preprototype hyperfiltration wash water recovery subsystem capable of processing the shower and laundry wash water of three to six crewmen for a period of 180 days without resupply. It will incorporate a low power feed pump, replaceable dual layer membrane hyperfiltration unit, urea-ammonia removal unit, a heated waste-storage tank, a replaceable filter, hydraulic damping components and associated ancillary equipment, controls, and instrumentation.

### 1.3 Program Organization

Lockheed maintained the prime responsibility for system development. Walden Research Division of ABCOR, Inc., was subcontracted to develop the dual membrane hyperfiltration module. The low-flow, high-pressure pump was developed by Pneu Devices, Inc., under subcontract to Lockheed.

## SECTION 2

HYPERFILTRATION SUBSYSTEM

After consideration of the available background data, a preliminary system concept was developed as a starting point for hardware development. This concept is shown schematically in Figure 2-1. The baseline system served as a basis for system studies during the program and was modified as required by new data evolved as part of the system and component development tasks.

2.1 Subsystem Operation

In operation of the baseline system, wash water flows periodically into the waste water storage tank as produced by shower usage and utility and clothes washing. The storage tank provides capacity to handle a portion of the daily consumption of the crew members. Table 2-1 presents a summary of the water use rates as well as soap usage and wash water composition. A liquid volume controller is used to control the wash water feed pump, energizing it when the liquid level in the storage tank reaches the high level point and de-energizing it when the liquid volume drops to the low limit. A bladder installed in the tank provides for zero gravity operation.

Tank pressure of  $103 \text{ kn/m}^2$  (15 psig) is used to overcome the pressure drop produced by the filter and to maintain a positive suction head on the feed pump. A heater and controller are provided to heat the incoming wash water quickly to the pasteurization temperature and maintain the system temperature when the pump is operating. High temperature warning and unsafe high temperature system shut-off are provided for safety. A sample valve is provided to allow measurement of the quality of the wash water both chemically and biologically and to drain the tank, if necessary.

A conductivity sensor installed at the tank discharge line is used as an indicator of system input loads. Two static,  $25\text{-}\mu\text{m}$  absolute filters installed in parallel at the outlet of the storage tank are used to remove large particles in the feed stream to increase membrane and component life. The parallel arrangement will allow one filter to be used while the other filter is in standby or being replaced without interrupting the system operation. A differential pressure gage and high pressure warning are provided to monitor filter performance and indicate when a filter change is required.

A positive displacement feed pump, installed after the filter, delivers wash water to the membrane module at a constant flow rate of  $3.2 \text{ cm}^3/\text{s}$  (0.05 gpm) with discharge pressure variations from  $4.1 \text{ Mn/m}^2$  (600 psig) to  $7.2 \text{ Mn/m}^2$  (1050 psig). The high and low pressure switches are used to shut the system down when the pump discharge pressure increases to  $8.3 \text{ Mn/m}^2$  (1200 psig) or when the pump suction pressure drops to  $6.9 \text{ kn/m}^2$  (1 psig). A relief valve at the discharge of the feed pump limits system pressure to  $7.6 \text{ Mn/m}^2$  (1100 psig). Pressure gages and high/low pressure signals indicate when the relief valve is open or the discharge pressure is below  $3.4 \text{ Mn/m}^2$  (500 psig).

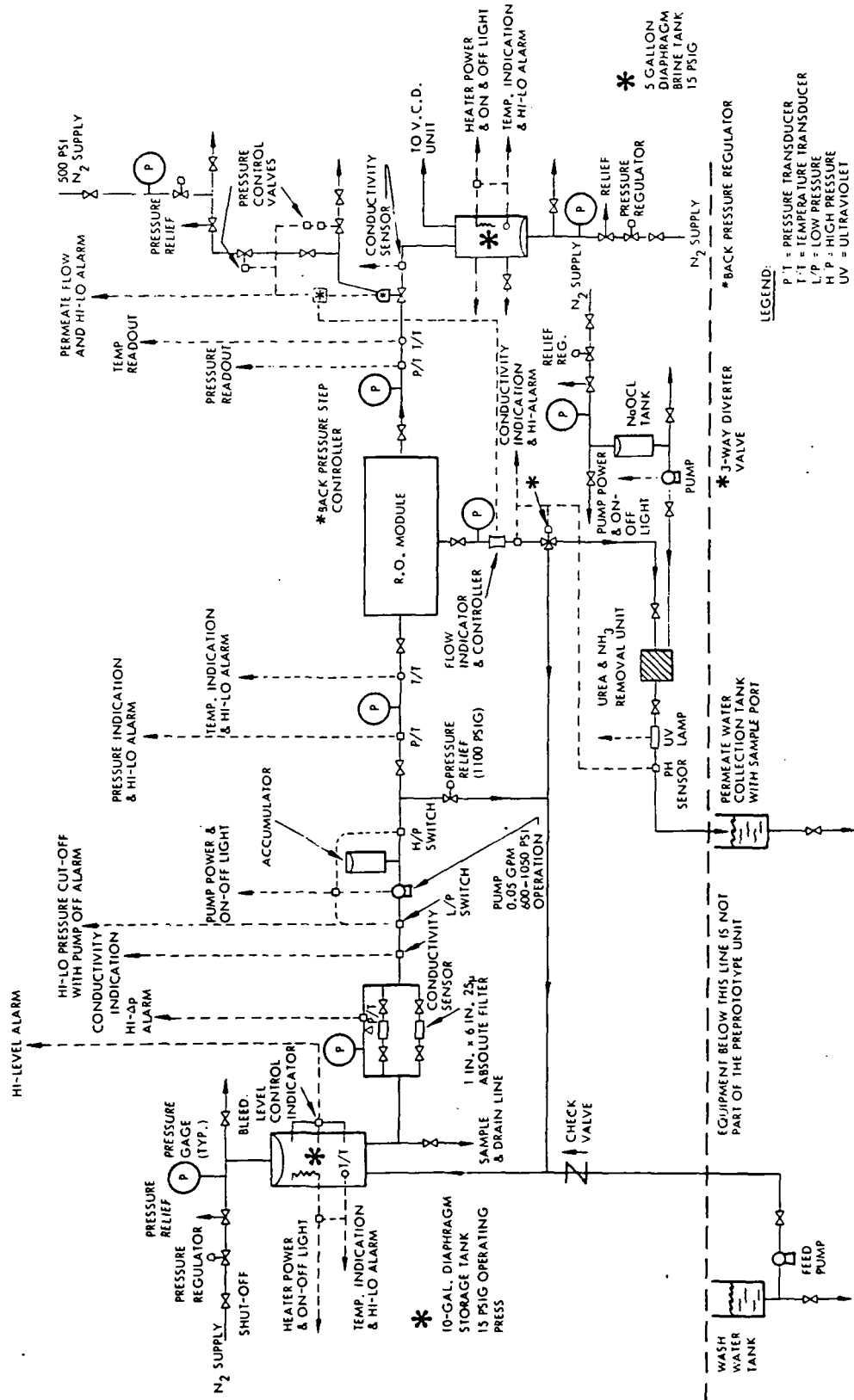


FIGURE 2-1  
PRELIMINARY HYPERFILTRATION SYSTEM SCHEMATIC

TABLE 2-1

WASH WATER SUMMARY - 6 MAN SYSTEM

## Water Usage

Shower	1 gal/man day
Hand Wash	$\frac{1}{2}$ gal/man day
Laundry	3 gal/man day
Total	27 gal/day for 6 men

## Soap Usage

Shower	1.2 gms/man day
Hand Wash	.4 gms/man day
Laundry	1.2 gms/man day
Total	16.8 gms/day for 6 men

## Water Composition - (LMSC Test Values)

TOC	170 ppm
TKN	21 ppm
NH <sub>3</sub> -N	9 ppm
pH	6 ppm

The membrane module is a single-pass design with 200 S.S. tubes, 0.2 cm in diameter and 35 cm long. At a flow rate of  $3.2 \text{ cm}^3/\text{s}$  (0.5 gpm), with the specified input composition and system pressures, the membrane module should provide a water recovery rate of approximately 90 percent. Thermocouples installed at the membrane module inlet and outlet provide an indication and warning if the temperatures fall below the pasteurization level.

The permeate water flow is monitored by a flow meter that is connected to a high/low flow level controller. When the permeate flow rate is lower than  $2.6 \text{ cm}^3/\text{s}$  (0.04 gpm), the low level controller will energize the back pressure step controller to increase permeate flow. When the permeate flow rate is at  $2.6 \text{ cm}^3/\text{s}$  (0.04 gpm), the back pressure regulator will hold the pressure. If the permeate flow rate increases to a value greater than  $2.6 \text{ cm}^3/\text{s}$ , the high level flowmeter controller will decrease the back pressure. The back pressure regulator is dome loaded with nitrogen gas. Timers are used to pulse the nitrogen gas into the regulator reference dome allowing the back pressure increase or decrease to be accomplished in small increments.

A diverter valve located in the permeate line is controlled by a conductivity cell and a pH sensor. If either permeate water conductivity or pH reaches an unacceptable level, the diverter valve automatically directs the permeate water back to the storage tank for reprocessing. A return to normal conductivity will automatically result in a return to normal position of the diverter valve. A manually operated pushbutton is used to reset the diverter valve to its normal flow position for pH control.

The removal of urea and ammonia is achieved by adding sodium hypochlorite to the permeate stream. The sodium hypochlorite feed pump is interlocked with the diverter valve. The pump operates only when the diverter valve is in the normal position. The hypochlorite feed pump will provide a constant volume flow designed to satisfy both high and low permeate water flow condition.

The concentrate tank provides a  $19\text{-dm}^3$  (5-gal) capacity. It will reject once daily the concentrate to the vapor compression unit for further processing. This tank is equipped with a high level alarm warning to prevent over pressurization.

## 2.2 Hardware Description

The major elements of the hyperfiltration subsystem, i.e., high pressure pump, the membrane module, urea-ammonia removal unit, pressure controls, and instrumentation are presented in the following sections.

The overall unit is presented pictorially in Figures 2-2 through 2-6. The system hardware design includes a welded extrusion frame that holds all of the components. All of the heated components or plumbing lines are insulated with most of the items being located in an insulated box. Pressure gages, controls and other displays are visible from the front of the unit. All equipment items are maintainable from either the front or back of the unit and all

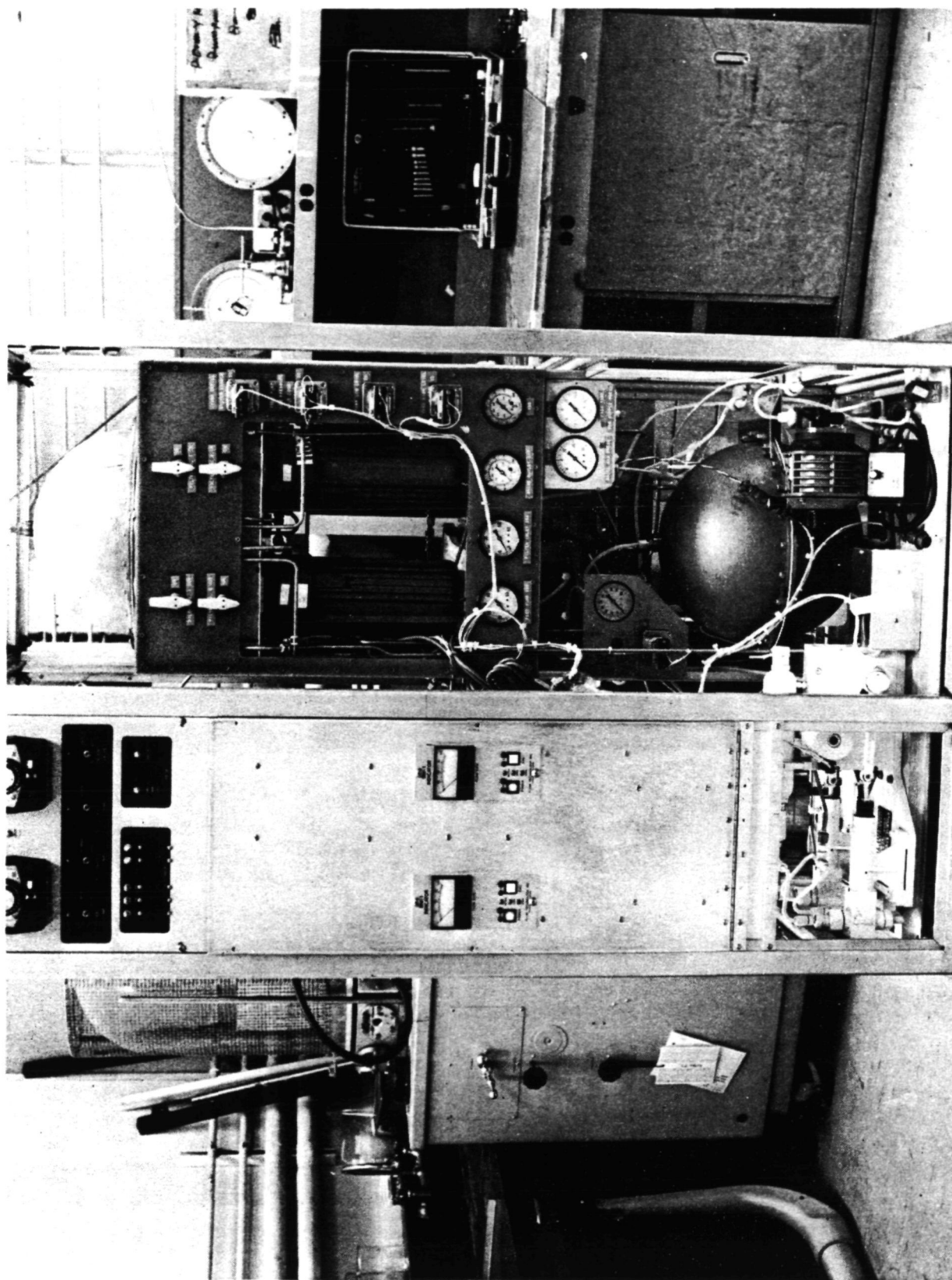


FIGURE 2-2 HYPERFILTRATION SYSTEM - FRONT VIEW

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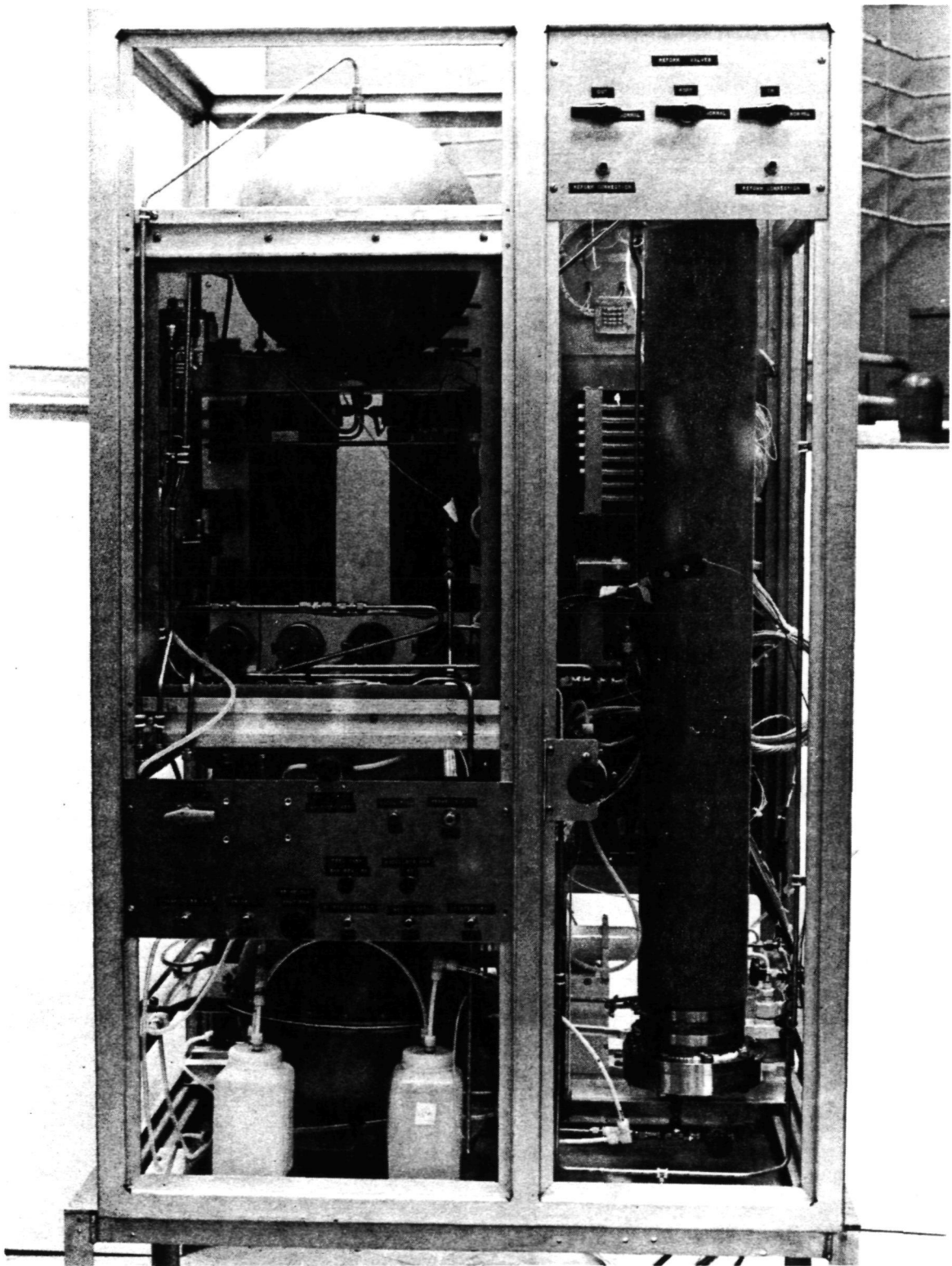


FIGURE 2-3 HYPERFILTRATION SYSTEM - BACK VIEW

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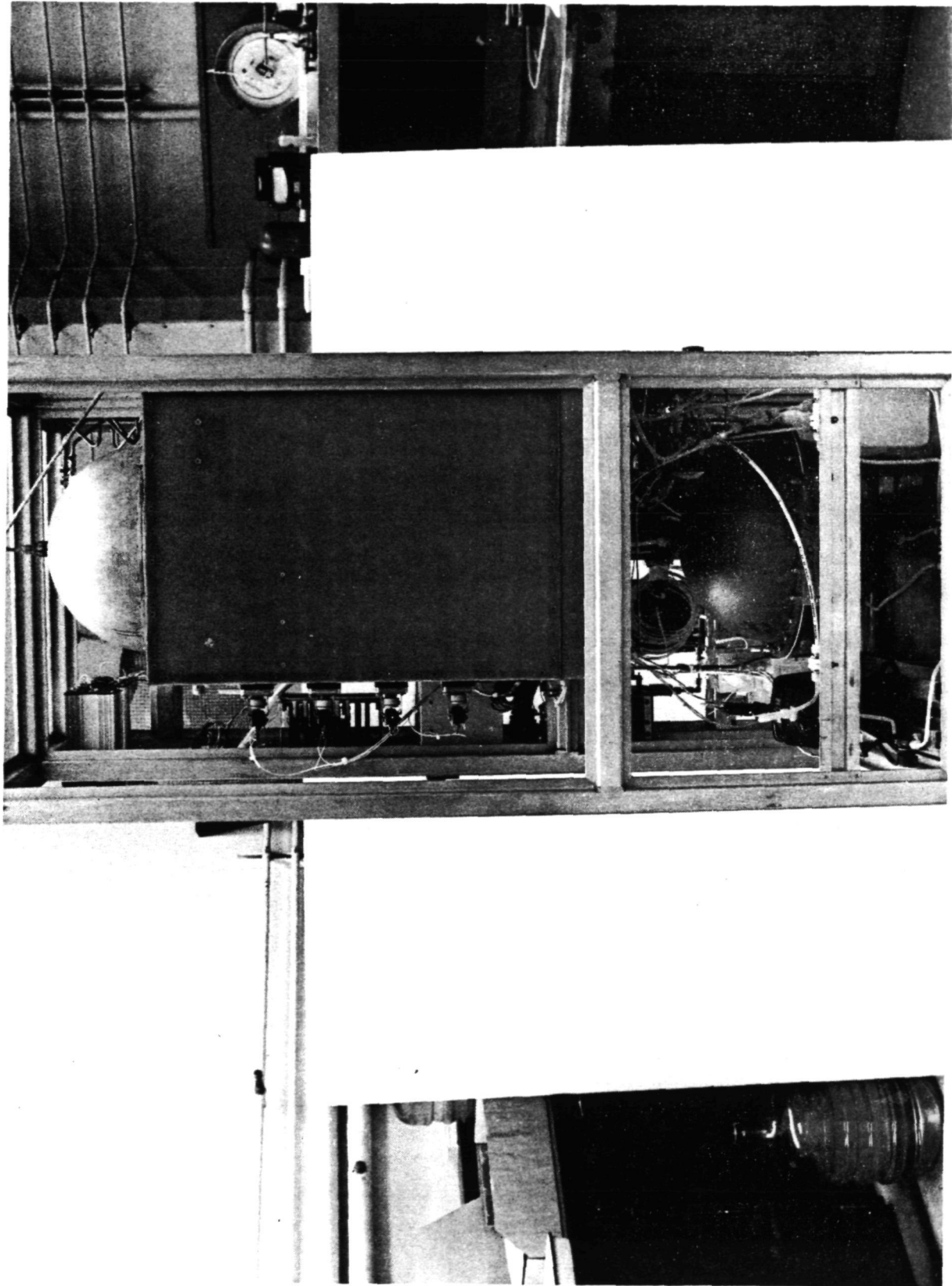


FIGURE 2-4 HYPERFILTRATION SYSTEM - LEFT SIDE VIEW

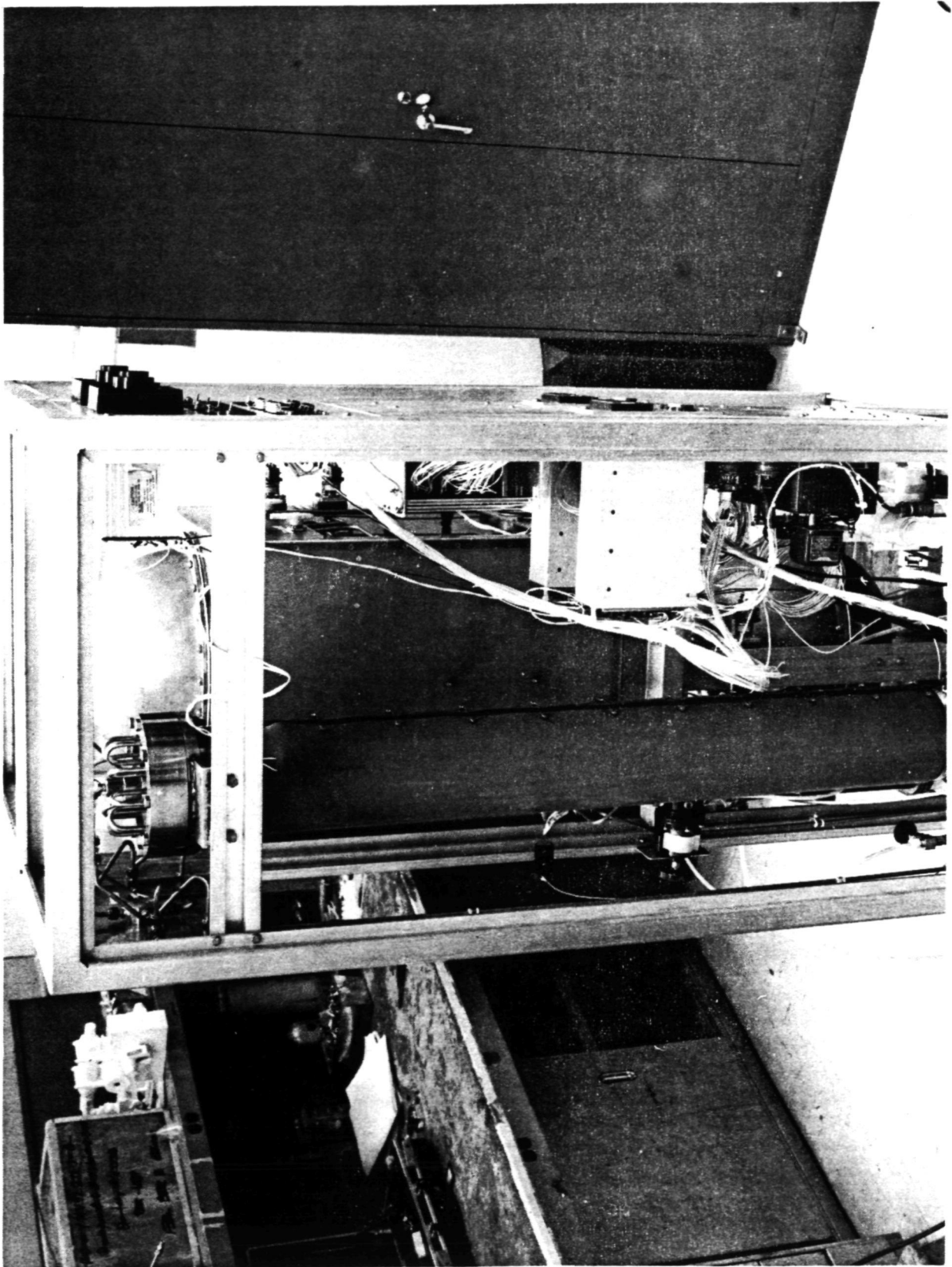


FIGURE 2-5 HYPERFILTRATION SYSTEM - RIGHT SIDE VIEW

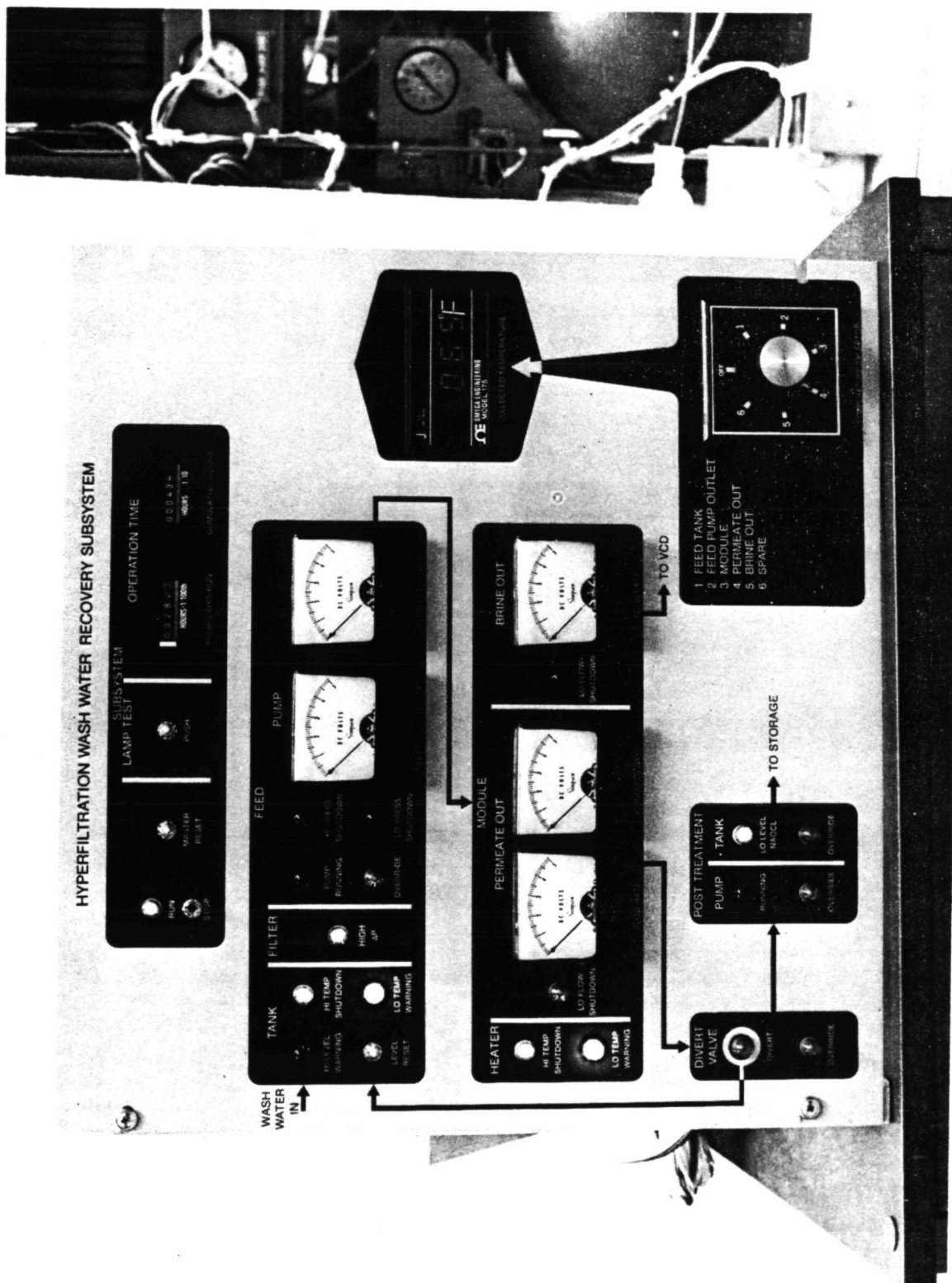


FIGURE 2-6 HYPERFILTRATION SYSTEM - REMOTE PANEL

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critical items such as filters and the viscojet assembly are easily replaceable.

The fluid and electrical interfaces are located at the back of the unit. The controls are fully automatic with status indicators and fault diagnostic lights. A manual override capability is provided for key items. An interface connector is provided for a remotely located display panel and computer interface for remote data acquisition.

A schematic of the final design is presented in Figure 2-7 with the schematic legend presented in Table 2-2 and parts list presented in Table 2-3.

A summary of the system operating parameters is presented in Table 2-4 and a summary of the relief valve and pressure switch set points is presented in Table 2-5.

The average power consumption of the subsystem is presented in Table 2-6.

### 2.2.1 High Pressure Pump

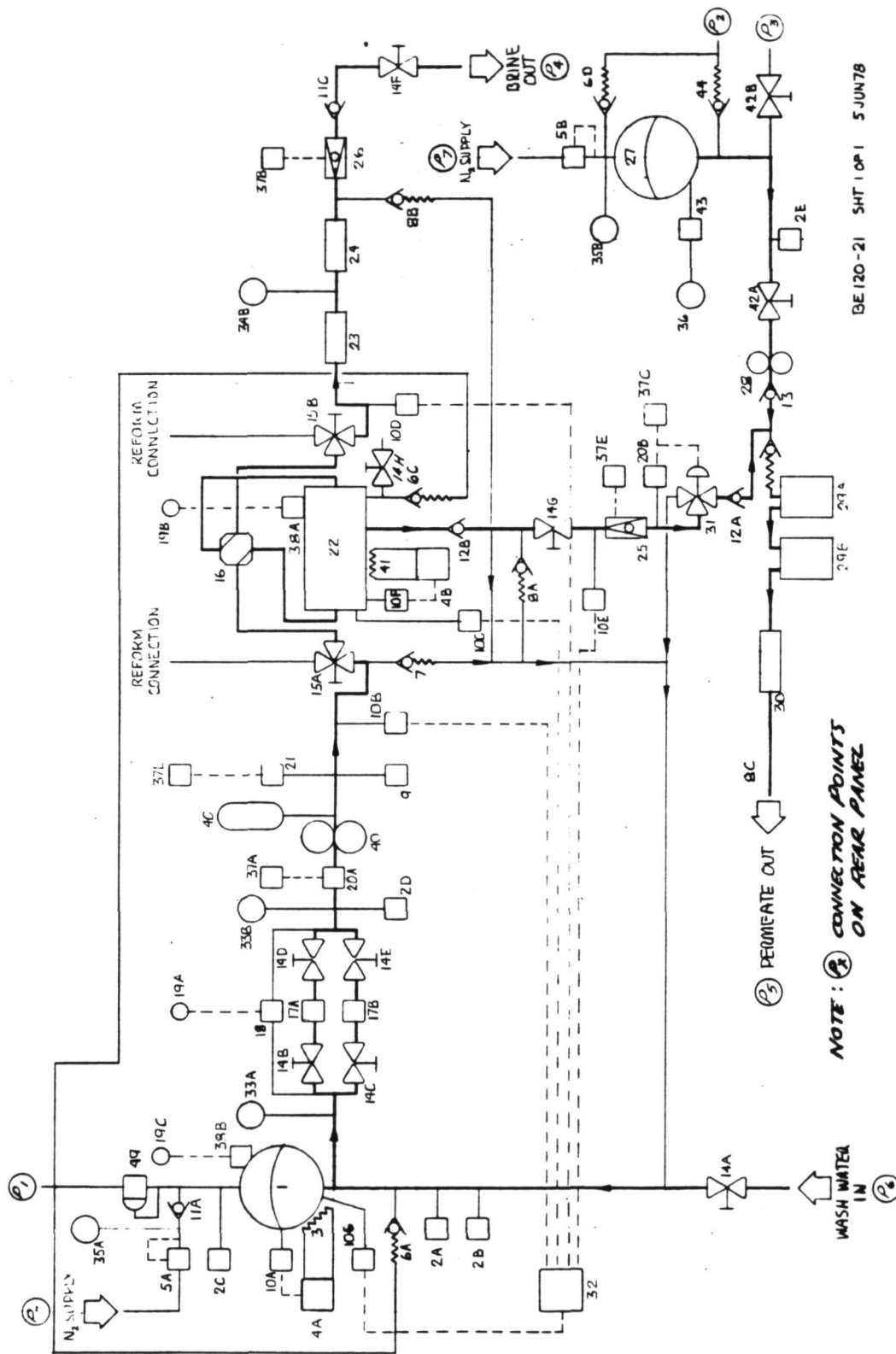
The selected pump is a duplex metering piston pump with a 400 Hz -3 phase Sawyer Industries motor, operating at 10,500 rpm and a spur gear reduction assembly with a reduction ratio of 121/1. The performance of this pump is 75 watts at 4.0 Mn/m<sup>2</sup> (650 psi) and 100 watts at 7.2 Mn/m<sup>2</sup> (1050 psi). This is an average power of 80 watts at the average system operating pressure of 5.8 Mn/m<sup>2</sup> (850 psi). It delivers 3.2 cm<sup>3</sup>/s (0.05 ± 0.004 gpm) over the total operating pressure range. A photo of the unit is shown in Figure 2-8.

### 2.2.2 Membrane Module

Because of the wide variation in operating conditions required for membrane formation and wash water processing, the design of the multi-tube module was subject to many demanding constraints. The module had to be capable of operating at:

- 70 kg/cm<sup>2</sup> Internal Tube Pressure
- 14 kg/cm<sup>2</sup> Back-Flush Pressure
- Very High and Very Low pH (During Membrane Stripping Procedure)
- High feed flow velocity (3-5 mps) with minimal pressure drop during membrane formation.
- Very low feed flow (0.2 lpm in, 0.02 lpm out) while maintaining adequate feed velocities (0.1-1.0 mps) during wash water processing.
- Very High Feed Temperature (74-90°C)

In addition, the module had to have a nominal wash water processing capacity of 273 lpd (72 gpd) when operated at 90% minimum water recovery, and be of minimal weight and volume. The module operational mode was to be continuous once-through (vs. continuous feed-and-bleed or batch) as this mode maximizes both product water quality and recovery while minimizing system power requirements (19, 20).



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FIGURE 2-7 HYPERFILTRATION SYSTEM FINAL SCHEMATIC

TABLE 2-2 HYPERFILTRATION SCHEMATIC LEGEND

<u>Item No.</u>	<u>Description</u>
1	Tank, Feed
2A,B,C,D,E	Adjustable Pressure Switch
3	Heater, Feed Tank
4A,B	Controller, Feed Tank Heater and Module Heater
5A,B	Pressure Regulator
6A,B,C,D	Pressure Relief Valve
7	Pressure Relief Valve (High Pressure)
8A,B,C	Pressure Relief Valve
9	Pressure Switch, Adjustable
10A,B,C,D,E,F,G	Thermocouple
11A,B,C	Check Valve
12A,B	Check Valve
13	Check Valve
14A,B,C,D,E,F,G	Shutoff Valve, Manual
15A,B	Ball Valve, 3 Way Manual
16	Ball Valve, 4 Way Manual
17A,B	Feed Filter, Cartridge and Housing
18	Pressure Switch, Differential
19A,B,C	Panel Light
20A,B	Conductivity Sensor
21	Pressure Transducer
22	Module, Hyperfiltration
23	Filter, Cartridge and Housing
24	Flow Controller (Viscojet)
25	Flow Meter (Permeate Out)
26	Flow Meter (Brine Out)
27	Tank, NaOCl
28	Metering Pump
29	Tank, Reaction
30	Carbon Bed
31	Solenoid Valve, Divert, 3 Way
32	Thermocouple Selector Switch and Digital Readout
33A,B	Pressure Gage
34A,B	Pressure Gage
35A,B	Pressure Gage
36	Pressure Gage
37A,B,C,D,E	Panel Meter (Readout)
38A,B	Temperature Switch
39	Bleed/Drain Valve
40	Feed Pump and Accumulator
41	Heater, Module
42A,B	Shutoff Valve
43	Bellows
44	NaOCl Relief Valve

TABLE 2-3 Hyperfiltration System Assy. Parts List

Quantity Req'd.	Part No. or Ident.	Description	Material Description or Note	Item No.
2	713339	Tank, Expulsion	Arrowhead Products	1
5	EIS-HI5PLS	Switch, Adj. Pressure	Barksdale	2
1	042678-5	Heater, Tank	Electroflex	3
2	65-8142	Controller, Heater	Love	4
2	70-230 ( $\frac{1}{2}$ -30)	Regulator, Pressure	Fairchild	5
4	SS-6R-4-10	Valve, Pressure Relief	-Nupro	6
1	5159T-4BB-1500	Valve, Pressure Relief	Circle Seal	7
3	SS-4CA-3	Valve, Pressure Relief	Nupro	8
1	C9612-3	Switch, Adj. Pressure	Barksdale	9
7	"J" Type, Iron Const.	Thermocouple	Lockheed (not shown this dwg)	10
3	SS-4C-1	Valve, Check	Nupro	11
2	SS-4C-1/3	Valve, Check	Nupro	12
1	SS-4C-10	Valve, Check	Nupro	13
7	SS-1K-S4	Valve, Manual Shut-off	Whitey	14
2	SS-43XS4	Valve, Manual 3-Way	Whitey	15
1	SS-43YF2(.125)	Valve, Manual 4-Way	Whitey	16
2	#10/MCY1001YCH2M	Filter, Assy.	Pall/Ametek	17
1	DPD1T-H1855	Switch, Differential Press.	Barksdale	18
		Indicator Light	On Display Panel	19
2	910-10T-C	Sensor, Conductivity	Balsbaugh	20
1	PA-822	Transduce, Pressure	Statham (within pump/accum. envelope)	21
1	ABC-5	Module, Hyperfiltration	Abcor	22
1	20666-6-250	Filter	Mectron	23



TABLE 2-3 Hyperfiltration System Assy. Parts List (cont'd)

Quantity Req'd.	Part No. or Ident.	Description	Material Description or Note	Item No.
1	VDCA4325730H	Controller Flow	Visco Jet	24
1	FTMN-.01 LJS	Flow Meter	Flow Technology	25
1	FTMN-.8 LJS	Flow Meter	Flow Technology	26
N.A.		Tank, Expulsion	Same as Item 1, See Item 1	27
1	10611-321	Pump, Metering	AMF Cuno	28
2	N/A	Tank, Reaction/Mix	Lockheed	29
1	N/A	Bed, Carbon	Lockheed	30
1	DV3144D2	Valve, 3-Way Solenoid	Fluorocarbon	31
		Thermocouple Sel. SW & Readout	On Display Panel	32
2	J6046	Gage, Pressure	Marsh	33
2	J6576	Gage, Pressure	Marsh	34
2	J4142	Gage, Pressure	Marsh (to be located after plumbing installed)	35
1	J4148	Gage, Pressure	Marsh	36
5		Meter, Panel	On Display Panel	37
1	M2-281-L140-04-05-3-1	Switch, Temperature	KLIXON	38
5	SS-4P-4	Valve, Bleed/Drain	Nupro (to be located after plumbing installed)	39
1	2347	Pump, Feed/Accumulator	Pneu Devices	40
1	N/A	Heater, Module	Electroflex	41
2	PVC-4V	Valve, Shutoff (plastic)	Nupro (to be located after plumbing - installed)	42
1	N/A	Bellows	Servometer	43
1	HC-6R-4-10	Valve, NaOCl Relief	Nupro	44



TABLE 2-3 Hyperfiltration System Assy. Parts List (cont'd)

Quantity Req'd	Part No. or Ident.	Description	Material Description or Note	Item No.
1	BE120-	Frame, Cabinet	Lockheed	45
1	BE120-	Control Panel Assy.	Lockheed	46
1	BE120-	Electronics Mounting Door	Lockheed	47
8	SS-400-61	Bulkhead Union	Swage Lok	48
1	10 BP	Back Pressure Regulator	Fairchild	49

TABLE 2-4

## SYSTEM OPERATING PARAMETERS

Module Operating Pressure	650-1050 psig
Process Rate	.05 $\pm$ .005 GPM
Module Operating Temperature	165 $\pm$ 5 <sup>o</sup> F
Recovery Ratio	NOM - .90 at 800 psig MAX - .92 at 650 psig MIN - .87 at 1050 psig
Inlet N <sub>2</sub> Pressure	15-150 psig
Inlet Wash Water	
Pressure	10-20 psig
Temperature	165 $\pm$ 5 <sup>o</sup> F
Permeate and Brine outlet pressure	0-10 psig
Regulated N <sub>2</sub> supply to feed and NaOCl tanks	5 psig
Feed tank operating pressure	5-9 psig
Feed tank capacity	5 gal.
Divert Conductivity (Adjustable)	2000 $\mu$ mo/cm
NaOCl flow rate (15% NaOCl)	.31 cc/min
NaOCl tank capacity	5 gal.

TABLE 2-5

## RELIEF VALVE AND PRESSURE SWITCH SET POINTS

<u>Item #</u>	<u>Function</u>	<u>Set Pres (psig)</u>
6A	System Liquid Relief	25
6B	Feed Tank N <sub>2</sub> Relief	9
6D	NaOCl Tank N <sub>2</sub> Relief	20
7	Pump Output Relief	1500
8A	Permeate from Module Relief	30
8B	Brine From Module Relief	30
13	Permeate Out Relief	10
44	NaOCl Tank Liquid Relief	30
2A	Feed Tank Full Sw.	10 A *
2B	Feed Tank Empty Sw.	4 D
2C	Feed Tank $\approx$ 1 Gal Sw.	8 A
2E	NaOCl Tank Empty Sw.	4 D
9	Pump High Pres. Sw.	1200 A
18	Filter $\Delta$ P Sw.	3 A

## Temperature Switch Set Points

Module & Tank Low Temperature	140°F D
Module and Tank High Temperature	205°F A

\*A = Ascending

D = Descending

TABLE 2-6

HYPERFILTRATION SYSTEMAVERAGE POWER CONSUMPTION (WATTS)

<u>OPERATING SYSTEM</u>	<u>TEST SYSTEM</u>	<u>FLIGHT SYSTEM ESTIMATE</u>
FEED PUMP	80	80
TANK MODULE TEMP CONTROLS	20	5
NaOCl METERING PUMP	52	10
CONTROLLER	35	5
DISPLAY PANEL	35	-
DIVERTER VALVE	<u>15</u>	<u>-</u> (2)
	222 (1)	100
 <u>STANDBY SYSTEM</u>		
TANK + MODULE HEATERS	50	20
 <u>AUXILIARY EQUIPMENT</u>		
WATER PREHEATER	800	-

(1) NaOCl PUMP AND DIVERTER VALVE DO NOT OPERATE SIMULTANEOUSLY

(2) USE LATCHING VALVE FOR FLIGHT

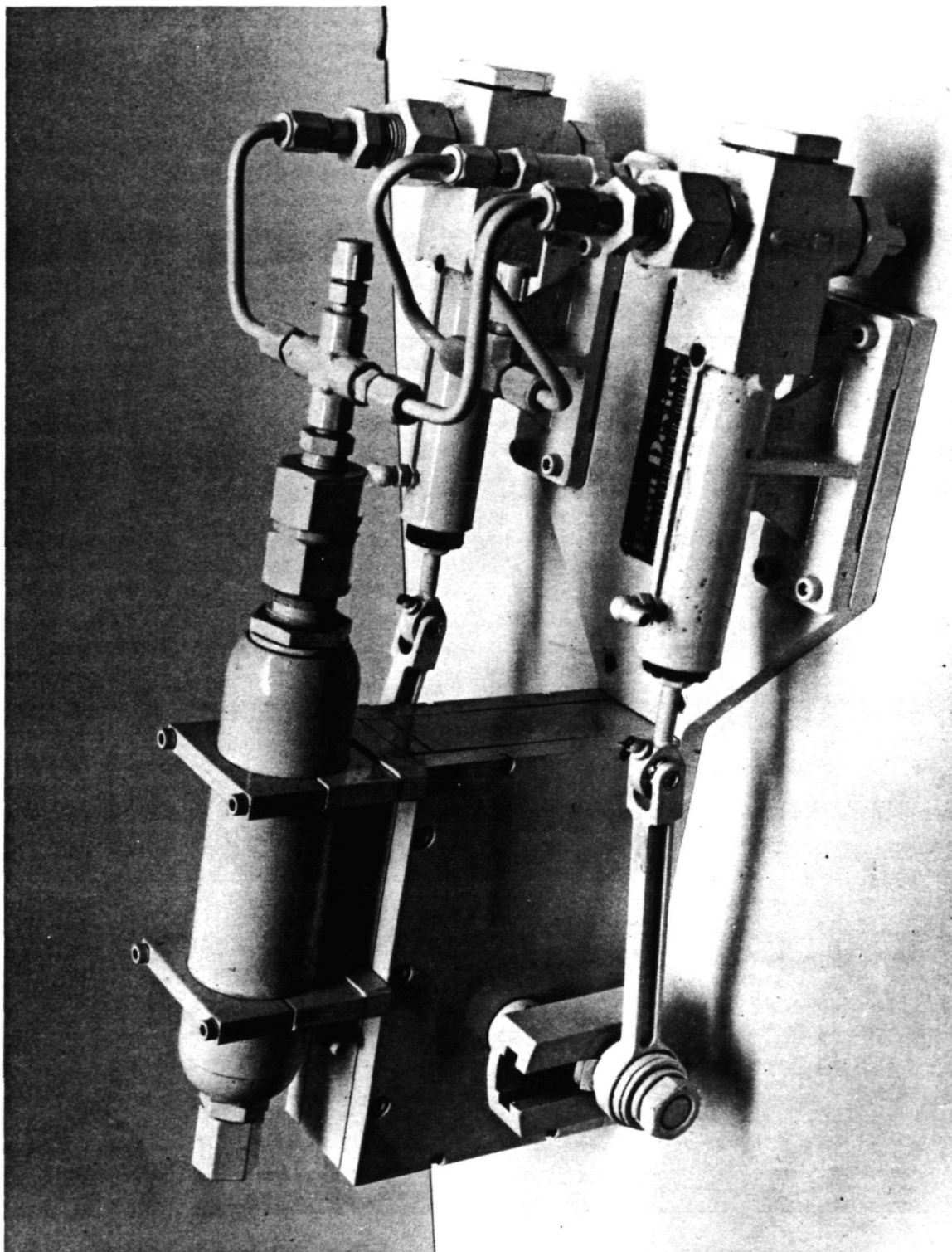


FIGURE 2-8 HYPERFILTRATION SYSTEM HIGH PRESSURE PUMP

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Based on the above constraints the multi-tube module was designed with a number of key features. First, all components were specified to consist of suitably pressure-resistant, pH-resistant, and temperature-resistant material (304 or 316 stainless steel, high-durometer viton or butyl rubber, etc.). Secondly, small flow-channel (2 mm i.d.) porous tubular supports were selected in order to maintain adequate velocity over the membrane surface during low-flow operation. Thirdly, in order to accommodate the wide range of flow rates while minimizing pressure drop, the module was designed to consist of a number of sub-modules which could be connected either in parallel configuration (for high-flow, membrane formation mode) or series configuration (for low-flow, wash water processing mode). Lastly, the module was designed to have sufficient membrane support surface area ( $0.3\text{m}^2$ ) to provide the specified product-water capacity.

Based on the above inputs the multi-tube module was designed and fabricated on a subcontract basis by Seavey, Inc., (Waltham, Mass.). A schematic of the two module header arrangements is shown in Figure 2-9 with a view of the housing, headers, and subassemblies shown in Figure 2-10.

The module consisted of nine four-tube subassemblies, with each tube having the following characteristics:

Type	Mott 0.5-micron Hypertube
Material	316 L Stainless Steel
Length	1.01 m
Inside Diameter	2.7 mm
Outside Diameter	8.8 mm
Inside Surface Area	86 $\text{cm}^2$

Tubing with 2.0 mm i.d. and 5.9 mm o.d. was originally requested as these were the dimensions of the tubing used in the single-tube tests. However, the manufacturer instead shipped the off-specification tubing described above and, due to time limitations, the larger tubing had to be used for the multi-tube module. As a result a partial redesign effort was required due to the larger o.d. More importantly, the larger i.d. resulted in a significant loss in internal feed velocity attainable at any given flow rate. Therefore the feed flow rates planned for wastewater processing (0.02-0.2 lpm) give a lower velocity range than would have been obtainable with the smaller diameter tubing (0.06-0.6 mps vs. 0.1-1.0 mps). These lower velocities could result in somewhat inferior membrane performance due to increased concentration polarization effects.

As indicated in Figures 2-9 and 2-10, the tubes in each subassembly were interconnected by welded U-bends, with the inlet and outlet connections of the subassemblies sealed into the distribution head by O-rings. The subassemblies were interconnected in either series or parallel flow by the appropriate manifolding.<sup>2</sup> Total inside surface area available for membrane formation was  $0.31\text{ m}^2$  ( $0.0344\text{ m}^2$  per subassembly).

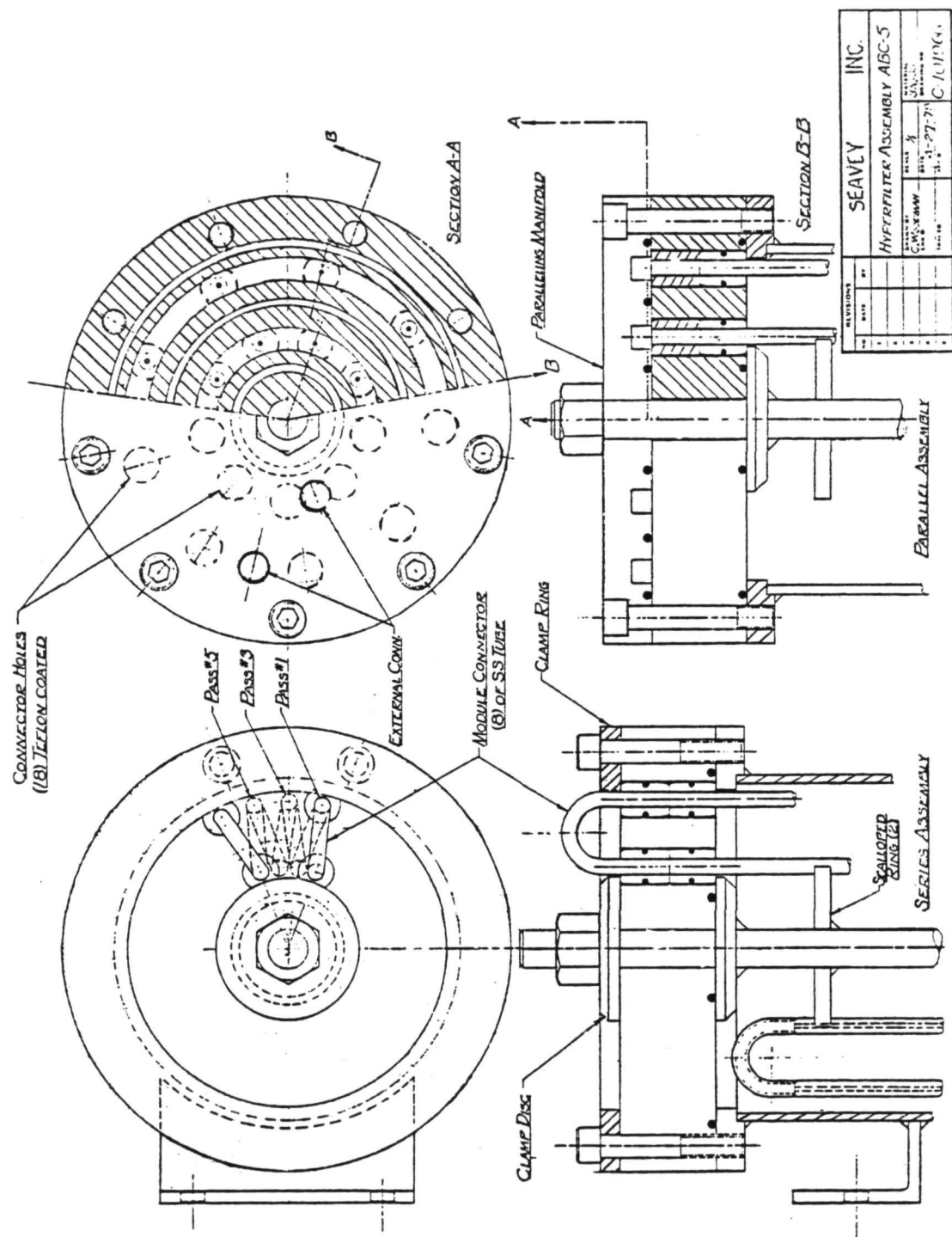


FIGURE 2-9 SCHEMATIC OF SERIES AND PARALLEL HEADER ASSEMBLIES FOR MULTI-TUBE MODULE

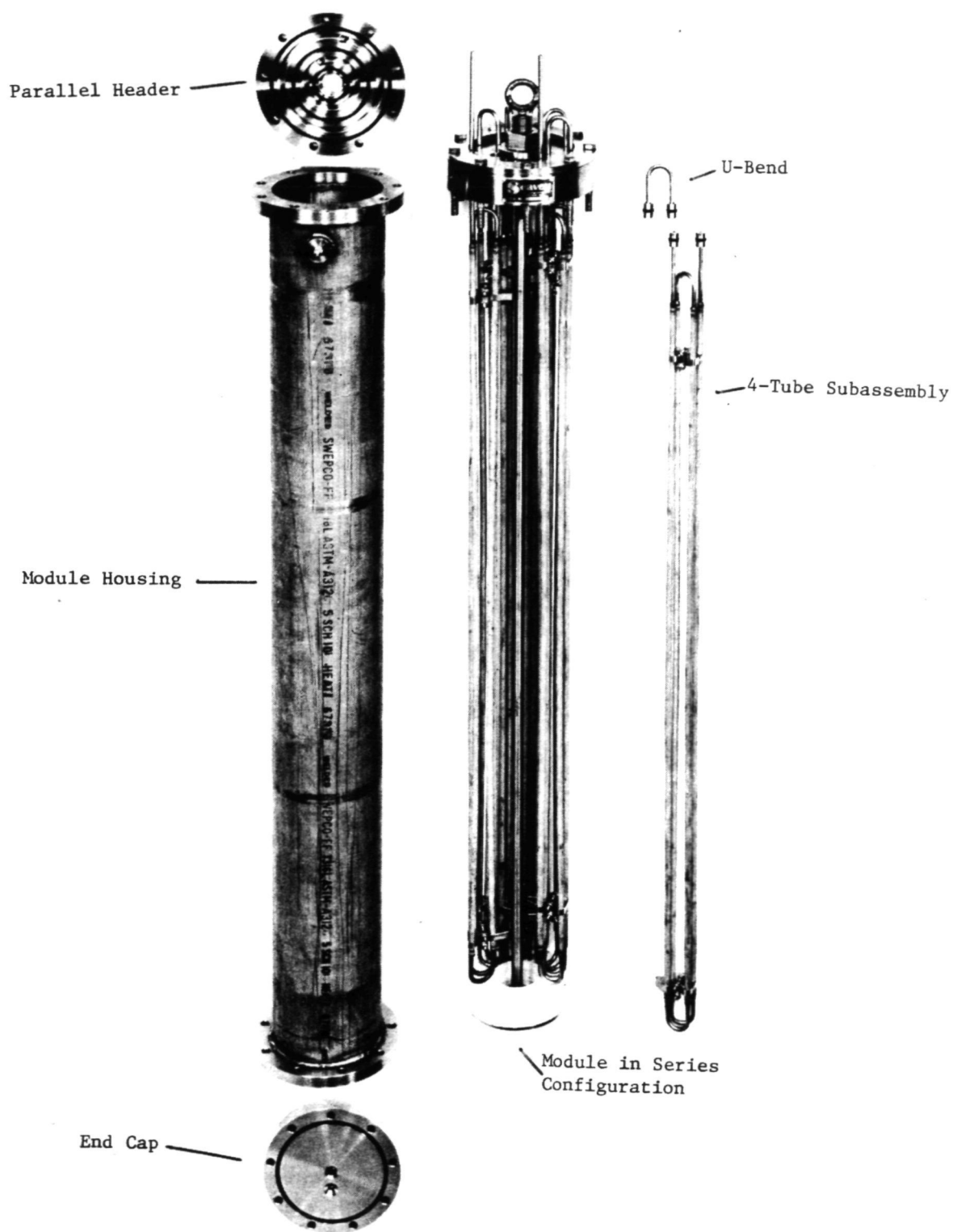


FIGURE 2-10 EXPLODED VIEW OF MULTI-TUBE MODULE



The final module shipping weight (including ZrO-PAA membrane and storage solution) was 49 kg. This figure is considered unacceptably high for a spacecraft application. However, the weight could be considerably reduced in future development from the preprototype to prototype stages, for example by:

- Replacing the heavy-duty stainless steel shell (required for membrane back-flushing) with a lightweight plastic shell.
- Replacing as many of the other stainless steel components as possible with lightweight plastic.
- Using thinner-walled stainless steel porous support tubing.\*

The total module volume was also high ( $\sim 0.02 \text{ m}^3$ ) considering the relatively small membrane area it contained. Considerable improvement could be achieved in this case through more compact header design or through use of novel (e.g., coiled) tubing configurations.

As the module is to be operated during wash water processing on a once-through basis at high (90%+) conversion, the feed must necessarily undergo significant concentration change as it proceeds down the long series path. Assuming constant membrane rejection as the feed concentration increases, the permeate concentration will increase proportionately and result in low apparent (or "observed") module rejection. To correct for this increase in feed concentration and determine the inherent (or "intrinsic") membrane rejection, the following equation may be used (19, 21):

$$R_I = 1 - \frac{\text{Log}(1 - Y(1 - R_0))}{\text{Log}(1 - Y)}$$

Where  $R_I$  = Intrinsic Rejection

$R_0$  = Observed Rejection

$Y$  = Conversion =  $\frac{\text{Module Permeate Flow Rate}}{\text{Inlet Feed Flow Rate}}$

The above equation is based on the assumption that membrane rejection remains constant as the feed concentration is increased. Although this assumption is faulty in the case of the ZrO-PAA membrane, the equation was nevertheless used throughout the program as a rough means of determining intrinsic membrane rejection.

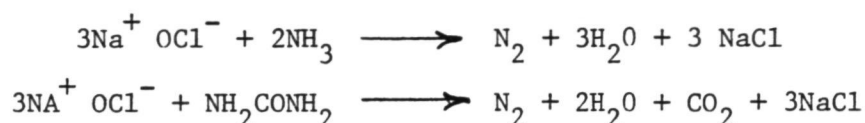
### 2.2.3 Urea-Ammonia Removal

During operation of the hyperfiltration module, a portion of the inlet ammonia and urea will pass through the membrane. The permeate ammonia level will likely be between 0 and 10 ppm and the urea concentration between 10 and 50 ppm. The urea, in the absence of a post-treatment step, will hydrolyze to produce additional ammonia. The hydrolysis step will occur rapidly at the temperature of

\* The off-specification tubing used for module fabrication weighed approximately 70% more than the tubing used in the single-tube tests.

the water in the process loop. In order to meet the allowable ammonia level of 5 ppm, a removal step for ammonia and urea is required.

Previous work conducted on the electro-chemical pretreatment of urine (22) has shown that both ammonia and urea are effectively removed by the addition of hypochlorite. Given sufficient hypochlorite, the reactions go essentially to completion as follows:



The results of these tests led to the selection of hypochlorite addition as the means of control of ammonia and urea in the treatment of wash water. Calculations show 0.92 gm-mols/day (0.00203 lb-mols/day) of hypochlorite are required to control the maximum projected contaminants. This amounts to less than 227 gm/day (0.5 lb/day) of 15 percent sodium hypochlorite solution. This material, when carefully stored, has a long storage life, is safe to handle, and is easily metered into the system. The metered addition of sodium hypochlorite to the product water is the simplest approach for the removal of ammonia and urea and thus was selected for the baseline system. Following addition of the hypochlorite, the mixture passes into a small hold tank which provides adequate time for reaction completion.

Metered addition of hypochlorite at a constant rate must be based on the maximum projected quantities of urea and ammonia and will result in overdose under low load conditions. Because carryover of unreacted, excess hypochlorite into the shower is unacceptable, reaction or decomposition of any excess must be accomplished before the water is returned to the shower storage tank. Laboratory tests have demonstrated that activated carbon can be used to catalytically decompose any excess hypochlorite.

The elements of the urea removal unit consist of a metering pump set nominally at 0.17 cc/min, a NaOCl supply tank, a carbon catalyst bed (3" dia x 12" long), and a static mixer. The catalyst bed is shown in Figure 2-11.

#### 2.2.4 Module Pressure Control

The module pressure control utilizes a viscojet (Lee Co.) to keep the flow of brine constant. This, in conjunction with a constant pump flow rate thus assures a fixed recovery ratio. Module pressure varies as required to obtain the proper permeate flow.

#### 2.2.5 Feed Filter

The elements of the filters are manufactured by the Pall Corporation and are constructed of polypropylene and have 547 in<sup>2</sup> of area. To minimize the accumulation of dirt on the visco jet, an element with a rating of 25 $\mu$  absolute, 5 $\mu$  nominal was selected. The filter housing is glass-filled nylon and is manufactured

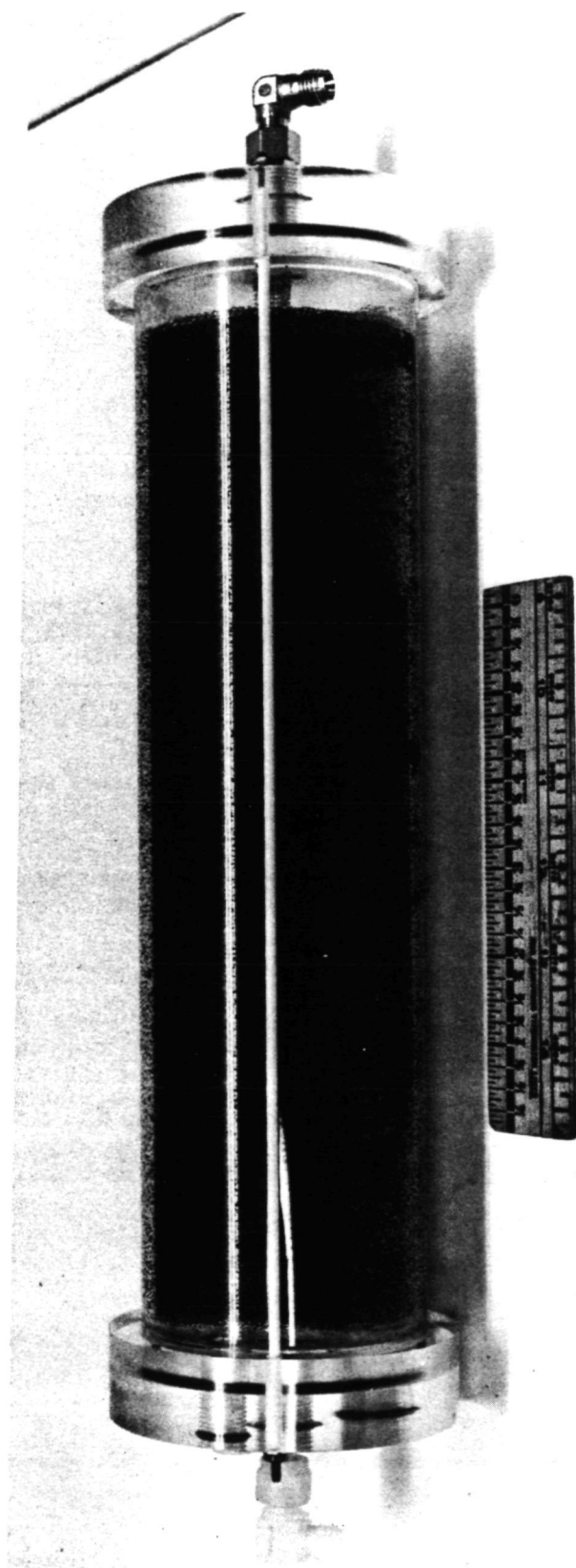


FIGURE 2-11 CATALYST BED

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by Ametek. Both housing and element are rated for service in excess of 200°F.

#### 2.2.6 Feed Tanks

Arrowhead Products of Los Alamitos, California was selected as the tank vendor. The tanks are spherical in shape as shown in Figure 2-12 and hold approximately 5 gallons. The bladders are food grade Viton. The NaOCl tank is internally coated with teflon.

#### 2.2.7 Controller, Control Panel, Instrumentation

The control and display functions and locations of items on the control and/or display panel are summarized in Table 2-7. The system is designed so that all essential control functions are provided at the unit on the control panel. All display functions are located on the remote display panel. In addition, at NASA's request, essential control switches and resets have been provided on the display panel. This will allow normal system operation using only the display panel. The system instrumentation summary is presented in Table 2-8. The first seven items will be supplied to the NASA computer through a separate connector. The controller logic diagram is presented in Table 2-9.

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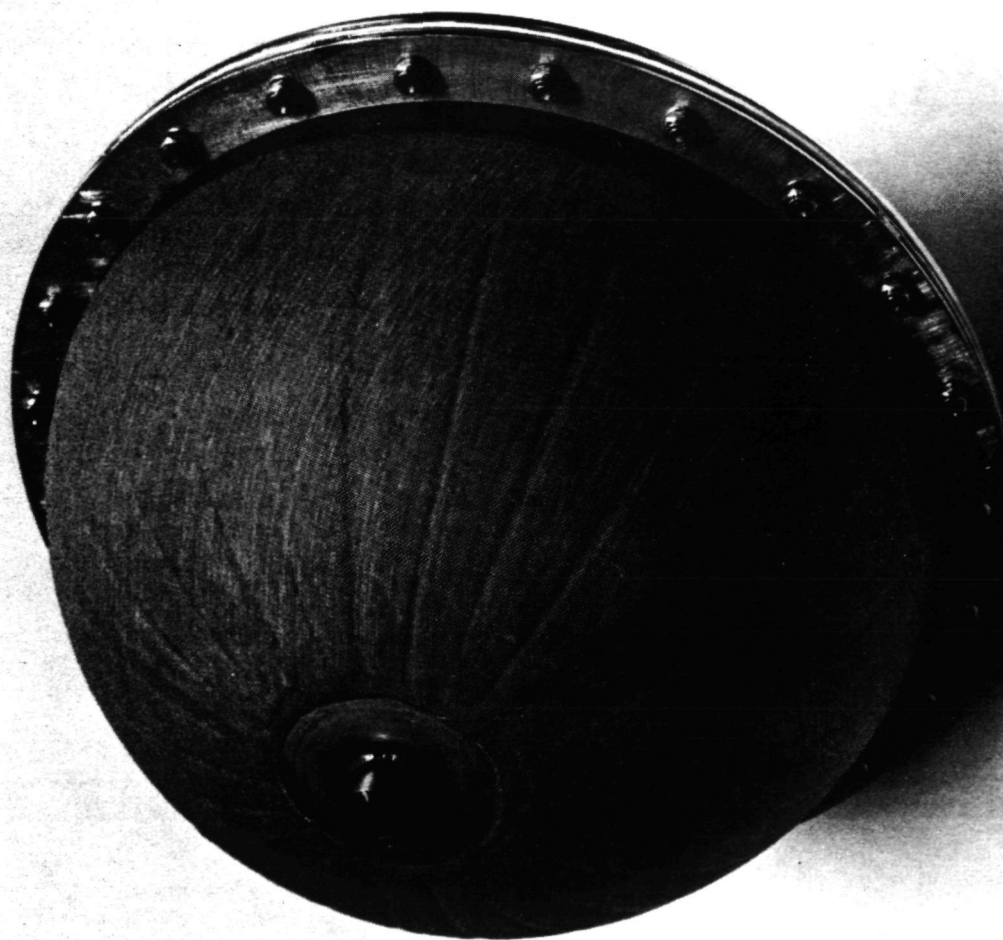


FIGURE 2-12 SPHERICAL TANK

TABLE 2-7 HYPERFILTRATION CONTROL/DISPLAY LOCATIONSCONTROL PANELOVERALL SYSTEM

1. System Power Circuit Breaker
2. Master Reset Switch
3. Lamp Test Switch

FEED TANK

4. Heater On/Off Switch
5. Control Temperature Set Pt
6. Control Temperature Readout
7. Low Temperature Warning Set Pt
8. High Temperature Shut Down Set Pt
9. High Temperatures Shut Down Reset Switch

FEED PUMP

10. Override/Auto Switch
11. Override Light
12. Feed Tank Reset Switch

DIVERT VALVE

13. Override/Auto Switch
14. Override Light

UREA AND AMMONIA REMOVAL

15. NaOCl Tank Low Override/Auto Switch
16. NaOCl Tank Low Override Light
17. NaOCl Pump Override/Auto Switch
18. NaOCl Pump Override Light

MODULE HEATER

19. Repeat Feed Tank Items 4 Through 9

DISPLAY PANELOVERALL SYSTEM

1. Lamp Test Switch
2. Run Time Meter
3. Cumulative Operation Time Meter
4. Main Start/Stop Switch
5. Master Reset
6. Main Start/Stop On/Off Light

FEED TANK

7. High Level Warning Light
8. Low Temperature Warning Light
9. High Temperature Shutdown Fault Light
10. Feed Tank Reset Switch

FEED FILTERS

11. High  $\Delta$  P Warning Light

FEED PUMP

12. Running Light
13. Low Suction Press Shutdown Fault Light
14. High Pump Press Shutdown Fault Light
15. Conductivity Readout
16. Temperature Readout
17. Override Light
18. Pressure Readout

BRINE OUT

19. Low Flow Shutdown Fault Light
20. Temperature Readout
21. Flow Readout

PERMEATE OUT

22. Low Flow Shutdown Fault Light
23. Conductivity Readout
24. Flow Readout

DIVERT VALVE

25. Valve Position Light
26. Override Light

UREA AND AMMONIA REMOVAL

27. NaOCl Tank Low Shutdown Fault Light
28. NaOCl Pump On Light
29. Pump Override Light
30. NaOCl Low Level Override Light

MODULE HEATER

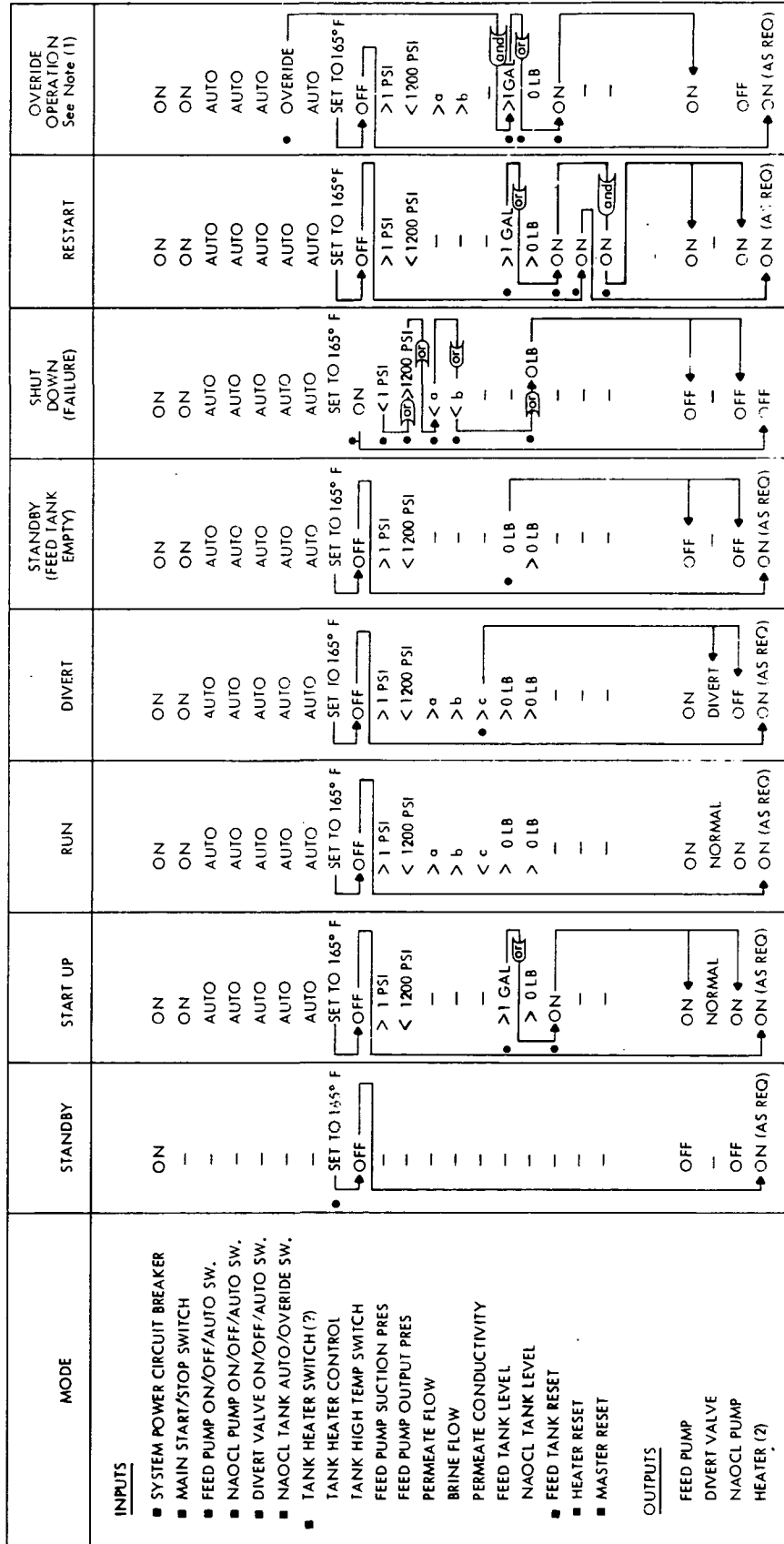
31. Repeat Feed Tank Items 8 through 9

TABLE 2-8 HYPERFILTRATION INSTRUMENTATION SUMMARY

DISPLAY CODE:  
 D Digital Tape  
 TP Test Control Panel  
 (Contractor-Supplied)  
 C CRT  
 S Strip Chart  
 PM Panel Meter  
 L Lamp Indicator

Subsystem: HYPERFILTRATION

<u>Parameter</u>	<u>Signal Type</u>	<u>SIGNAL LEVEL</u>	<u>Display Range</u>	<u>Display</u>
Brine Flow	Analog	0-5 VDC	0-.008 GPM	PM, TP, C
Permeate Flow	Analog	0-5 VDC	0-.08 GPM	PM, TP, C
Feed Conductivity	Analog	0-5 VDC	TBD	PM, TP, C
Permeate Conductivity	Analog	0-5 VDC	TBD	PM, TP, C
Pump Pressure	Analog	0-5 VDC	0-1500 PSI	PM, TP, C
Temperature (1 of 5)	Analog	1 NV/ <sup>°</sup> F	0-300 <sup>°</sup> F	PM, TP, C
Valve Divert	Digital	5 VDC		L, TP, C
Low Suction Pressure Shutdown	Digital			L, TP
High Pump Pressure Shutdown	Digital			L, TP
NaOCl Low Level Shutdown	Digital			L, TP
Brine Low Flow Shutdown	Digital			L, TP
Permeate Low Flow Shutdown	Digital			L, TP
Feed Pump On	Digital			L, TP
NaOCl Pump On	Digital			L, TP
Feed Tank Low Temperature	Digital			L, TP
Module Low Temperature	Digital			L, TP
High Feed Filter $\Delta$ P	Digital			L, TP
High Feed Tank Level	Digital			L, TP
NaOCl Low Level Override	Digital			L, TP
Feed Pump Override	Digital			L, TP
Valve Override	Digital			L, TP
NaOCl Pump Override	Digital			L, TP
Totalizing Timer	Digital		0-100,000 Hr	PM, TP
Run Timer	Digital		0-1000 Hr	PM, TP
Module Heater On	Digital			L, TP
Module Heater Off	Digital			L, TP
Module Overtemperature	Digital			L, TP
Module Temperature	Analog		0-300 <sup>°</sup> F	PM, TP
Module Low Temperature Warning	Digital			L, TP
Feed Tank Heater On	Digital			L, TP
Feed Tank Heater Off	Digital			L, TP
Feed Tank Overtemperature	Digital			L, TP
Feed Tank Temperature	Analog		0-300 <sup>°</sup> F	PM, TP
Feed Tank Low Temperature Warning	Digital			L, TP



NOTES:

(1) FEED PUMP NAOCL PUMP &amp; DIVERT VALVE CAN BE MANUALLY OVERRIDDEN AT ANY TIME

(2) MODULE HEATER CONTROL IS IDENTICAL TO TANK HEATER CONTROL

a = .035 GPM  
 b = .0035 GPM  
 c = 2000 μ/CM

● MASTER INITIATOR  
 ■ MANUAL SWITCH

TABLE 2-9 HYPERFILTRATION CONTROLLER LOGIC DIAGRAM



## SECTION 3

DEVELOPMENT TESTING

Development testing was conducted on the key subsystem elements. Two sub-contractors conducted development tests on their deliverable hardware: single element and module testing was conducted by ABCOR, Inc., Wilmington, Mass; feed pump testing was performed by Pneu Devices, Inc., (PDT) Goleta, California. At Lockheed, development testing was conducted on the urea/ammonia removal unit and the pressure control device.

3.1 Membrane Formation Systems and Procedures3.1.1 Hyperfiltration Test System

The test system used to evaluate single-tube porous supports in the membrane formation experiments is shown in Figure 3-1. With minimal modifications essentially the same system was subsequently used to evaluate the multi-tube module.

Referring to Figure 3-1, the feed solution was withdrawn from a 100-liter polyethylene feed tank and passed through the supports by the high-pressure feed pump. Either a plunger-type pump (FWI Triplex P-200A or Gaulin Triplex 100 CGD) or a diaphragm pump (Yarway Cyclophram) was used. Flow was controlled by needle valves after each support and by a bypass loop, with the flow through each support indicated by a rotameter. To minimize pump pulsations a nitrogen-filled accumulator was installed just downstream from pump discharge. A high-pressure switch, pressure-relief valve, and low-pressure switch were installed to protect the system in case of accidental over-pressurization or feed loss. Feed temperature was monitored and controlled automatically by the appropriate switches, a solenoid valve, and a heat exchanger installed in the bypass loop.

The test system was designed with an emphasis on minimizing generation of contaminants which could interfere with the sensitive membrane formation process. The system was constructed from stainless steel, polyethylene, or other chemically resistant materials wherever possible in order to withstand salt-induced corrosion and attack by the pH extremes encountered during the membrane formation and stripping experiments. In addition, stagnant areas were avoided through careful system design so as to allow efficient cleaning.

Prior to passing through the supports the feed solution was filtered by either of two high-pressure filters. During membrane formation a stainless steel strainer (140- or 230- micron, Nupro No. SS-6TF) was generally used. During performance evaluations with salt solution or during membrane stripping experiments a 25-micron borosilicate depth filter (Balston 95 S) was used. This finer filter was also tried during membrane formation but without success due to rapid plugging by the hydrous zirconium oxide.

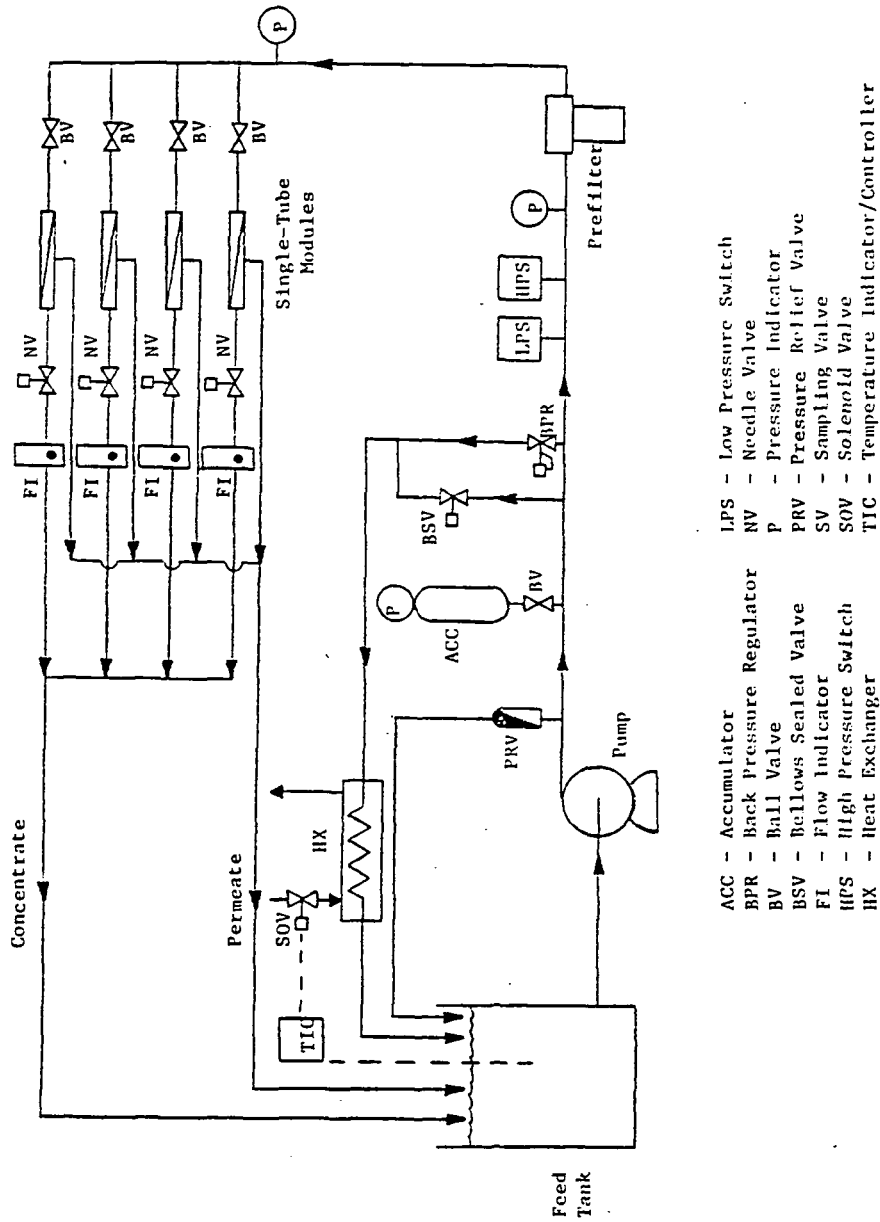


Figure 3-1 Flow Schematic of Hyperfiltration System  
Used to Evaluate Single-Tube Modules

### 3.1.2 Porous Supports

The characteristics of the porous tubular supports chosen for initial membrane formation tests are shown in Table 3-1. The stainless steel supports (Mott Metallurgical Corp., Farmington, Conn.) included two types with 0.5-micron pore-size ratings and one with a 2.0-micron rating. The 0.5-micron "Hypertube" is made through a proprietary process resulting in a somewhat different pore structure from that of the standard 0.5-micron tube.

The stainless steel supports had the following necessary characteristics for this program:

- Sufficiently small pore size to allow ZrO-PAA membrane formation.
- Small diameter (0.2 cm), which permits adequate linear feed velocities at very low flow rates.
- Chemical inertness (required for pH and temperature extremes).
- Excellent durability.

One disadvantage of this type of material for Spacecraft applications is its large weight: support-volume ratio ( $0.3\text{--}0.4 \text{ g/cm}^3$ ) relative to other support materials such as ceramic or carbon. Also, the absolute pore sizes of the Mott supports may actually be up to ten times larger than the manufacturer's designations, which refer to the minimum particle size retained under cross flow (23). Therefore the absolute pore sizes are probably much greater than the maximum recommended value of 1 micron (19, 23). As will be discussed below, this can make ZrO-PAA membrane formation relatively difficult without the prior use of filteraid.

The 0.3-micron ceramic support (Selas Corporation, Flotronics Division, Huntingdon Valley, Pa.) had the advantages of very small pore size, small diameter, and a small weight: volume ratio ( $0.07 \text{ g/cm}^3$ ). In addition, these tubes have generally exhibited somewhat higher membrane flux rates than the stainless steel tubes. However, their relatively poor durability - as evidenced by a significant rate of tube rupture experienced in another program (19) - make these supports particularly unsuitable for spacecraft applications. The ceramic tubes were therefore used during the single-tube testing for control purposes only, and were not considered in the final selection process for development into a multi-tube module.

Efforts were made to locate sources of alternative tubular support materials having characteristics superior to those of the Mott tubes (i.e., smaller pore size or smaller weight: volume ratio). However, the results of a brief survey (See Table 3-2) indicated no suitable alternative. Each of the candidate materials had at least one significant disadvantage, such as large pore size, large diameter, or commercial inavailability, which quickly eliminated it from further consideration.

TABLE 3-1 CHARACTERISTICS OF POROUS TUBULAR SUPPORTS SELECTED  
FOR SINGLE-TUBE MEMBRANE FORMATION TESTS

Manufacturer	Material Type	Flow Configuration	Manufacturer's Pore-Size Designation (microns)	Length (cm)	Inside Diameter (cm)	Outside Diameter (cm)
Mott Metallurgical	316 stainless steel	internal	0.5	45	0.2	0.6
Mott Metallurgical	316 stainless steel	internal	0.5 ("hypertube")	45	0.2	0.6
Mott Metallurgical	316 stainless steel	internal	2.0	45	0.2	0.6
Selas Flotronics	ceramic	external	0.3	35	0.2	0.5

TABLE 3-2 CHARACTERISTICS OF ALTERNATIVE  
POROUS TUBULAR SUPPORTS

Manufacturer	Material Type	Available Pore Sizes (microns)	Inside Diameter (cm)	Outside Diameter (cm)	Comments
Pall Trinity	316 stainless steel	2-22	3.8	--	max. operating pressure 18 kg/cm <sup>2</sup>
Wolverine Tube Division Universal Oil Products	316 stainless steel	2-8	1.3	--	requires filteraid precoat to form ZrO-PAA membrane
Pacific Sintered Metals	bronze	5-130	2.5-15.2	--	
Electro Division Ferro Corporation	ceramic	60-1300	--	2.5-10.2	not resistant to strong alkaline solutions
Owens-Illinois	ceramic	--	--	--	production discontinued
Rev-O-Pak Division Ferro Corporation	ceramic	--	--	1.6	requires cellulose acetate overwrap to form ZrO-PAA membrane
Wisconsin Porcelain	ceramic	>40	--	--	
Union Carbide	carbon	--	--	--	individual tubes not commercially available

For the single-tube membrane formation tests the Mott and Selas supports were inserted in stainless steel housings and sealed with O-rings. The housing designs were similar to those used previously by Clemson University (19). The stainless steel supports were operated using internal feed flow, whereas the ceramic supports were operated with external feed flow to reduce the chances of tube fracturing.

### 3.1.3 Membrane Formation Procedure

The ZrO-PAA membrane formation procedure used during this program was based on those developed previously at Clemson (24, 25, 19) and Oak Ridge National Laboratory (ORNL) (26). The procedure consisted of the following four basic steps:

1. System Cleaning
2. Deposition of Filteraid
3. Deposition of Hydrous Zirconium Oxide
4. Deposition of Polyacrylic Acid

A brief description of the membrane formation procedure follows. Additional details are given in Appendix A.

Thorough cleaning of the hyperfiltration test loop, considered essential to the formation of high-quality membranes, was performed prior to each run by successive washes with 1 M NaOH and 1 M HNO<sub>3</sub> at 30-50°C. Membrane stripping to allow reuse of the stainless steel supports was also achieved by this procedure (described below). Previously unused stainless steel supports were inserted into the loop during the HNO<sub>3</sub> wash to remove corrosion products.

Following a thorough water rinse the membrane formation procedure was initiated. Based on recommendations by Clemson no filteraid was initially used in the single-tube tests. However, such a step was later found to be necessary for successful membrane formation on the stainless steel supports. In the single-tube tests, the procedure used was simply to circulate a 38-liter, 25-ppm dispersion of carbon-black filteraid (Cabot Regal SR or Sterling R) past the supports for 30 minutes at 25-30°C, 28-42 kg/cm<sup>2</sup>, 4.6 mps inlet feed velocity. 40 ppm ZrO(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (Alfa Division, Ventron Corp.) and 0.05 M NaNO<sub>3</sub> were then added, the pH adjusted to 4.0, and the operating pressure raised to 70 kg/cm<sup>2</sup> as soon as possible. Once the conductivity rejection had increased to 30-50%, 50 ppm polyacrylic acid (PAA, Rohm and Haas Acrysol A-3) was added and the pH adjusted to 2.0. Finally the pH was raised one unit at a time, waiting 30 minutes at each intermediate level, to a final pH of 7.0. If membrane performance was not yet satisfactory the pH excursion was repeated with or without an additional dosage of PAA. This step often resulted in rejection improvement, although at the expense of reduced flux.

For membrane formation on the multi-tube module a slightly modified procedure was used. Because the module surface area was 20-100 times the largest areas used previously in the single-tube tests, it was believed that an increase in either

the feed volume or in the concentrations of the various membrane constituents would be required. To check this, the membrane formation conditions recently used at Clemson and ORNL were compared to those used in this program. The data (see Table 3-3) indicated that the general procedure for membrane formation on larger surface areas was to maintain the feed constituent concentrations within previously accepted levels while increasing the feed volume to some degree. At Clemson, where most of the recent dynamic-membrane module work has been performed, the resultant ratios of formation-chemical mass to support surface area have been:

Carbon Black	3.6-10.8 g/m <sup>2</sup>
Zirconyl Nitrate	8.1-17.7 g/m <sup>2</sup>
Polyacrylic Acid	5.4-28.0 g/m <sup>2</sup>

Accordingly, the feed concentrations proposed for module membrane formation at Walden were kept approximately the same as in the single-tube tests, while the feed volume was raised from 38 to 100 liters. The resultant proposed mass/surface-area ratios (5.4 g/m<sup>2</sup> carbon black, 13.0 g/m<sup>2</sup> zirconyl nitrate, and 16.4 g/m<sup>2</sup> polyacrylic acid) each fell within the ranges used at Clemson.

Once the module membrane formation tests were underway, it became clear that the transition from single-tube to multi-tube membrane formation would not be straightforward. Therefore, in attempts to improve membrane performance the concentrations of all three feed constituents were eventually increased at various stages in the formation process. The final conditions used are compared to those originally proposed in Table 3-4.

Rejection determinations during membrane formation were based on feed and permeate conductivity measurements using a YSI Model 31 conductivity bridge. pH values were measured with an Analytical Measurements Model 73 digital meter.

#### 3.1.4 Membrane Removal Techniques

Re-use of the stainless steel supports was exercised throughout the program by chemical removal of the ZrO-PAA membranes. Thermal regeneration at 260°C has also been suggested (19,20), but this method was not considered by Clemson or ORNL to be as useful as the chemical means available.

The most efficient membrane-removal technique used in this program was to back-flush the membranes at the maximum permissible pressure using the following feed solutions in sequence:

1. RO-treated tap water (15 minutes, once-through basis, 16-20°C).
2. 1 M NaOH (1 hour, recirculation basis, 30-50°C).
3. RO-treated tap water (as in "1").
4. 1 M HNO<sub>3</sub> and 0.1% oxalic acid (1 hour, recirculation basis, 30-50°C).

TABLE 3-3 COMPARISON OF MEMBRANE FORMATION CONDITIONS  
USED AT ORNL, CLEMSON, AND WALDEN

Constituent	ORNL	Clemson	Walden	
			Single-Tube Tests	Proposed for Module Tests
carbon black (Regal SR or Sterling R)				
concentration (ppm)	10	10 - 100	25	16.5
feed volume(liters)	50	100 - 189	38	100
support surface area (m <sup>2</sup> )	0.008	0.28 - 0.93	0.003 - 0.015	0.31
mass/surface-area ratio (g/m <sup>2</sup> )	59.2	3.6 - 10.8	64.6 - 349	5.4
zirconyl nitrate (ZrO(NO <sub>3</sub> ) <sub>2</sub> ·nH <sub>2</sub> O)				
concentration (ppm)	40	25 - 75	40	40
feed volume (liters)	50	100 - 189	38	100
support surface area (m <sup>2</sup> )	0.008 - 0.23	0.28 - 0.93	0.003 - 0.015	0.31
mass/surface-area ratio (g/m <sup>2</sup> )	25.8 - 236	8.1 - 17.7	103 - 558	13.0
polyacrylic acid (Acrysol A-3)				
concentration (ppm)	50	50	50	50
feed volume (liters)	50	100 - 189	38	100
support surface area (m <sup>2</sup> )	0.008 - 0.23	0.28 - 0.93	0.003 - 0.015	0.31
mass/surface-area ratio (g/m <sup>2</sup> )	10.8 - 295	5.4 - 28.0	129 - 699	16.4



TABLE 3-4 MULTI-TUBE MODULE MEMBRANE FORMATION CONDITIONS  
(FEED VOLUME 100 LITERS, SUPPORT SURFACE AREA 0.31 m<sup>2</sup>)

Constituent	Formation No. 01		Formation No. 02	
	Proposed	Actual	Proposed	Actual
carbon black (Sterling R) concentration (ppm) mass/surface-area ratio (g/m <sup>2</sup> )	16.5	24.8	33.0	33.0
	5.4	8.1	10.8	10.8
zirconyl nitrate concentration (ppm) mass/surface-area ratio (g/m <sup>2</sup> )	40	120	200	400
	13.0	39.1	65.2	130.5
polyacrylic acid concentration (ppm) mass/surface-area ratio (g/m <sup>2</sup> )	50	250	200	750
	16.3	81.5	65.2	244

### 5. RO-treated tap water (as in "1").

Back-flush pressures in the single-tube tests were maintained at  $14 \text{ kg/cm}^2$ . For the multi-tube module the back-flush pressures were generally restricted to just  $3\text{--}6 \text{ kg/cm}^2$  due to limited pump capacity after the first few seconds of membrane stripping.

Cleaning efficiency was determined after each stripping cycle through measurement of water flux rates under standard conditions ( $21 \text{ kg/cm}^2$ ,  $20^\circ\text{C}$ , with 8- or 25-micron depth prefiltration). Under these conditions the flux rates for fresh stainless steel supports were in the range of  $60,000\text{--}90,000 \text{ l/m}^2\text{-hr}$ .

No attempts were made to re-use the ceramic tubes, as this support type was not considered a viable option for multi-tube module development.

## 3.2 Washwater Processing System and Procedures

### 3.2.1 Hyperfiltration Test System

At the conclusion of the module membrane formation experiments the hyperfiltration system was modified to allow washwater processing at high temperature ( $81^\circ\text{C}$ ). All plastic components, such as the polyethylene feed tank and PVC suction line, were replaced with stainless steel equivalents. The following components were then installed:

- Low-flow concentrate flow meter ( $0\text{--}180 \text{ cc/min}$ ).
- Low-flow concentrate needle valve.
- Feed, concentrate, and permeate sample valves.
- 440-micron high-pressure strainer.
- 2-kilowatt tank heater.
- Heater temperature probe.
- Fiberglas insulation around module, tank, valves, and piping.

A schematic and photograph of the washwater processing system are shown in Figures 3-2 and 3-3 respectively.

### 3.2.2 Synthetic Washwater Composition

The formulation used for preparation of synthetic wash water was provided by LMSC (see Table 3-5). All chemicals were reagent-grade quality except for the laboratory-grade sodium lauryl sulfate powder. RO-treated tap water was used for makeup water.

### 3.2.3 Washwater Analytical Methods

The methods and instruments used for analysis of wash water constituents are given in Table 3-6.

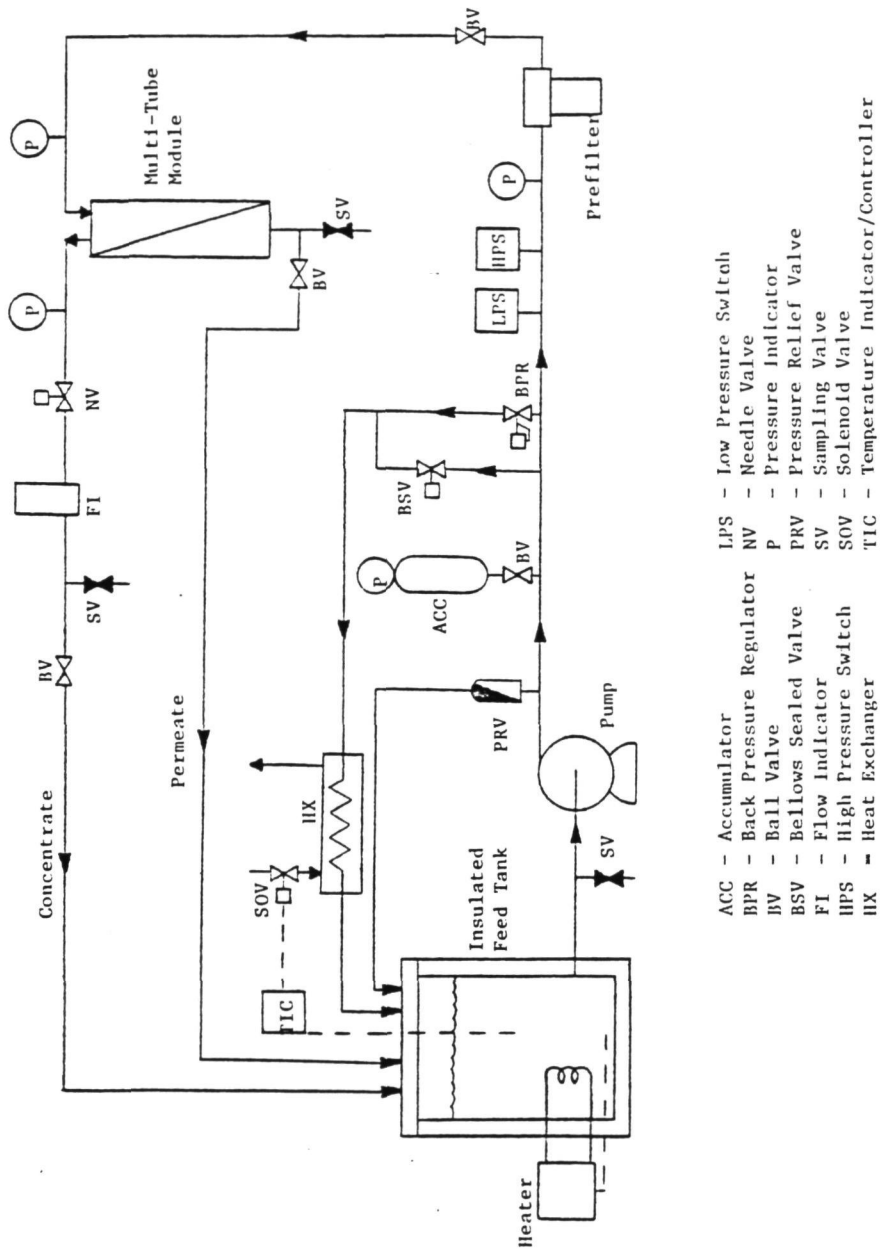


FIGURE 3-2 Flow Schematic of Hyperfiltration System  
Used for Washwater Processing

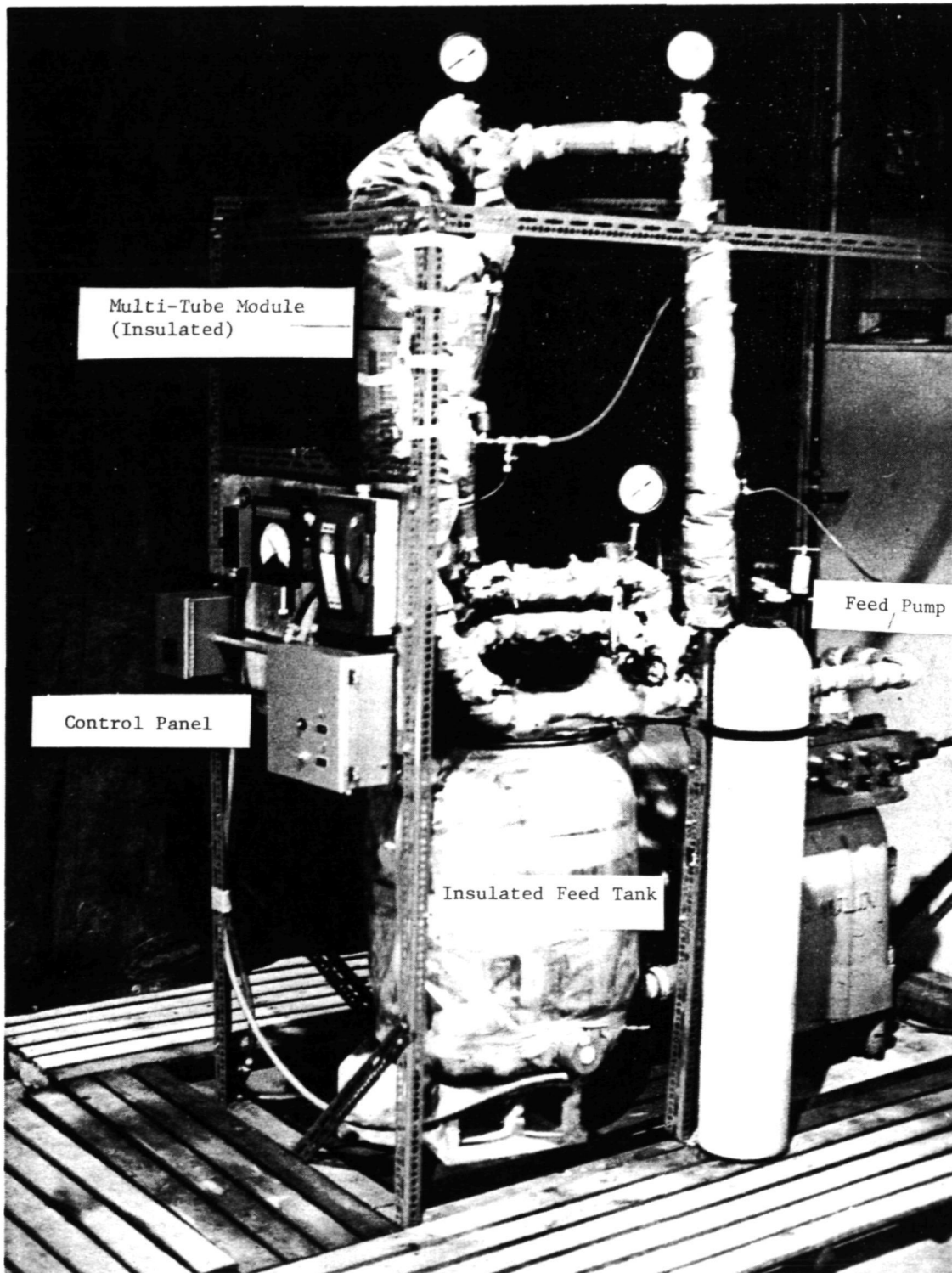


FIGURE 3-3 PHOTOGRAPH OF HYPERFILTRATION SYSTEM USED  
FOR WASHWATER PROCESSING

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TABLE 3-5 FORMULATION FOR SYNTHETIC WASHWATER

Reagent	Reagent State	Amount Added per Liter
ammonium hydroxide	29% aq. solution	0.093 cc
dextrose	anhydrous powder	0.008 g
lactic acid	85% aq. solution	0.152 g
potassium hydroxide	pellets (contain 10-15% water)	0.047 g
sodium chloride	crystal	0.183 g
sodium lauryl sulfate	powder	0.368 g
urea	crystal	0.064 g

TABLE 3-6 METHODS USED FOR ANALYSIS OF  
SYNTHETIC WASHWATER CONSTITUENTS

Constituent	Method	Instrument
ammonia	selective ion electrode	Orion 701 A
urea	Total Kjeldahl Nitrogen* concentration less ammonia concentration	--
total organic carbon	combustion/flame ionization detection	Dohrmann DC-50
total solids	gravimetric**	--
turbidity	turbidimeter	Hach 2100 A
conductivity	conductivity bridge	YSI Model 31
pH	digital pH meter	Analytical Measurements Model 73

\* Procedure Number 421 in "Standard Methods for the Examination of Water and Waste Water", APHA, 14th Ed., 1975.

\*\* Procedure Number 208 in "Standard Methods for the Examination of Water and Waste Water", APHA, 14th Ed., 1975.

### 3.3 Multi-Tube Module Test History

Subsequent to the membrane formation experiments the module was evaluated in two sets of parametric and washwater processing tests. The first set of tests, which were relatively brief, were followed by several membrane regeneration attempts in efforts to improve observed rejection levels. A more detailed parametric run and a longer washwater run (50 hours) were then conducted in the second set of tests.

In summary the module test history was as follows:

1. Parametric Evaluation with Sodium Nitrate, Run No. 1.
2. Evaluation with synthetic Washwater, Run No. 1.
3. Membrane Regeneration Attempts
4. Parametric Evaluation with Sodium Nitrate, Run No. 2.
5. Evaluation with Synthetic Washwater, Run No. 2.

At the end of these tests the module was shipped to LMSC for incorporation in the preprototype washwater recovery subsystem.

### 3.4 Membrane Formation Results with Single Tubes

A total of sixteen ZrO-PAA membrane formations were conducted with single tubes in order to develop technique and select the support type to be used in module fabrication. Thirteen formations were conducted without use of filteraid, three formations with filteraid. Based on earlier studies (20, 21) a target conductivity rejection level of 88% was chosen. Although membrane flux was considered to be less critical, a minimum range of 30-50  $l/m^2$ -hr was selected as a reasonable goal. The results of the single tube tests are summarized below. Detailed hyperfiltration performance data are given in Appendix B.

#### 3.4.1 Performance Without Filteraid

The use of filteraid to improve membrane formation results for stainless steel supports was not considered necessary early in the program, as previous results at Clemson (19) had indicated that acceptable performance could be obtained without it. This was subsequently demonstrated in a training session conducted at Clemson for Walden personnel, where the following data were generated for small surface-area (65-170  $cm^2$ ) supports without filteraid (0.05M  $NaNO_3$ , 70  $kg/cm^2$ , 40°C, 3.8-4.0 mps feed velocity):

	Rejection (%)	Flux $l/m^2$ -hr)
Mott SS 0.5	88-90	23-25
Selas Ceramic 0.3	90-92	95-129

Although the flux rates obtained with the stainless steel supports were significantly less than those obtained with the ceramic supports, the conductivity rejections equaled or exceeded the target level of 88%. These results, combined with suspicions that filteraid could contribute to membrane instability (19), led to the decision not to use filteraid in initial experiments at Walden.

The results of the first two membrane formation experiments conducted at Walden

were encouraging. Using the same support materials as those used at Clemson (Mott Standard 0.5-micron stainless steel plus Sela ceramic 0.3-micron "control"), the following performances were obtained (0.05M  $\text{NaNO}_3$ , 60-67  $\text{kg/cm}^2$ , 30°C, 4.6 mps):

	Rejection (%)	Flux <sub>2</sub> ( $\text{l/m}^2\text{-hr}$ )
SS 0.5 $\mu$	89-92	36-64
Ceramic Controls	80-88	36-62

The performance of the 0.5-micron stainless steel supports was considered excellent as (1) conductivity rejections were in excess of the desired 88% level, and (2) in contrast to the results observed at Clemson the flux rates were as high as those obtained with the ceramic supports.

Mott 2.0-micron stainless steel supports were also tried in the first two runs, but membrane formation rates were exceedingly slow. Flux rates after 50 minutes of zirconium oxide application were still in excess of 40,000  $\text{l/m}^2\text{-hr}$ , versus the 400-500  $\text{l/m}^2\text{-hr}$  level reached at the same stage for the 0.5-micron tubes. As it was thus apparent that the 2.0-micron supports were too "open" to allow adequate membrane formation, tests with these supports were discontinued. The 0.5-micron Hypertubes were not included in these initial tests as they had not yet been received from Mott; these were subsequently included in testing beginning with Formation No. 08.

Unfortunately, after the first two experiments it became increasingly difficult to form acceptable  $\text{ZrO-PAA}$  membranes. Much longer time periods were required to achieve adequate  $\text{ZrO}$  membrane performance (30-50% conductivity rejection at 200-300  $\text{l/m}^2\text{-hr}$ ), and the final  $\text{ZrO-PAA}$  rejections were consistently less than the desired 88% level. Repetition of the PAA application step (a so-called "regeneration" step) was useful in improving rejection but only to a certain extent. Performance ranges obtained during Formation Nos. 03-13 were as follows (0.05 M  $\text{NaNO}_3$ , 60-70  $\text{kg/cm}^2$ , 30°C, 4.6 mps):

		Rejection (%)	flux <sub>2</sub> $\text{l/m}^2\text{-hr}$
<u>WITHOUT</u> <u>REGENERATION</u>	SS 0.5 $\mu$	43-68	42-106
	SS 0.5 $\mu$ Hypertube	48-63	50-76
	Ceramic Controls	22-78	29-133
<u>WITH</u> <u>REGENERATION</u>	SS 0.5 $\mu$	66-85	32-58
	SS 0.5 $\mu$ Hypertube	65-81	32-40
	Ceramic Controls	64-85	26-87

The considerable difference in performance levels seen between Formations 01-02 and Formations 03-13 was eventually traced to variability in the membrane formation feed solutions. In the first two formations considerable fouling of the feed was observed in the form of iron hydroxide and worn pump packing



material, i.e., Teflon particulates, asbestos fibers, and/or graphite fibers. The fouling was most severe in Formation No. 01. As it was believed that any of the observed contaminants could result in less-than-optimum hyperfiltration performance and perhaps contribute to membrane instability, efforts were subsequently made to remove their sources (e.g., corrosion-prone carbon-steel fittings, pump packings with poor pH resistance, scored plungers). As a result the feed solutions used in Formations 03-13 were considerably cleaner than those used in the first two formations. However, these actions had the reverse effect of that desired in that the ZrO-PAA membranes appeared to form at much slower rates, with final performances much inferior to those originally obtained with contaminated feeds. In Formation No. 12, there was no observable rust or packing material in the feed, as all non-stainless fittings had been replaced and the Yarway diaphragm pump was used instead of the Gaulin plunger pump. Yet, as shown in Figure 3-4 total membrane formation time was nearly double the 4-6 hour period expected under normal circumstances (26), and final rejections were only 50-78%.

It was therefore concluded at this point that (1) the contaminants present in the first two runs had served as necessary aids, and not as deterrents, to the membrane formation process; and (2) use of a relatively controlled filteraid pretreatment step would be highly beneficial for ZrO-PAA membrane formation on the 0.5-micron stainless steel supports. The need for such a step was later confirmed through a careful review of the literature (23).

As shown above, there was no significant difference in hyperfiltration performance between membranes formed on the "standard" and "Hypertube" 0.5-micron supports. The ceramic control performed better than the stainless steel supports if a clean feed solution was used, with occasional exceptions due to mechanical problems such as seal slippage or tube fracturing. When contaminated solutions were used, the above-mentioned filteraid effect gave the stainless steel supports a decided rejection advantage over the ceramic support.

#### 3.4.2 Performance with Filteraid

The addition of a filteraid step to the membrane formation process resulted in a dramatic improvement in performance for the stainless steel supports. Use of 25 ppm Cabot Sterling R carbon black (average particle size 75 millimicrons) in Formation Nos. 14-16 resulted in the following ZrO-PAA flux and rejection ranges (0.05 M  $\text{NaNO}_3$ , 70  $\text{kg}/\text{cm}^2$ , 30°C, 4.6 mps):

	REJECTION (%)	FLUX <sub>2</sub> ( $\text{l}/\text{m}^2\text{-hr}$ )
SS 0.5 $\mu$	90-93	56-94
SS 0.5 $\mu$ Hypertube	91-94	51-84
Ceramic Control	85-87	56-103

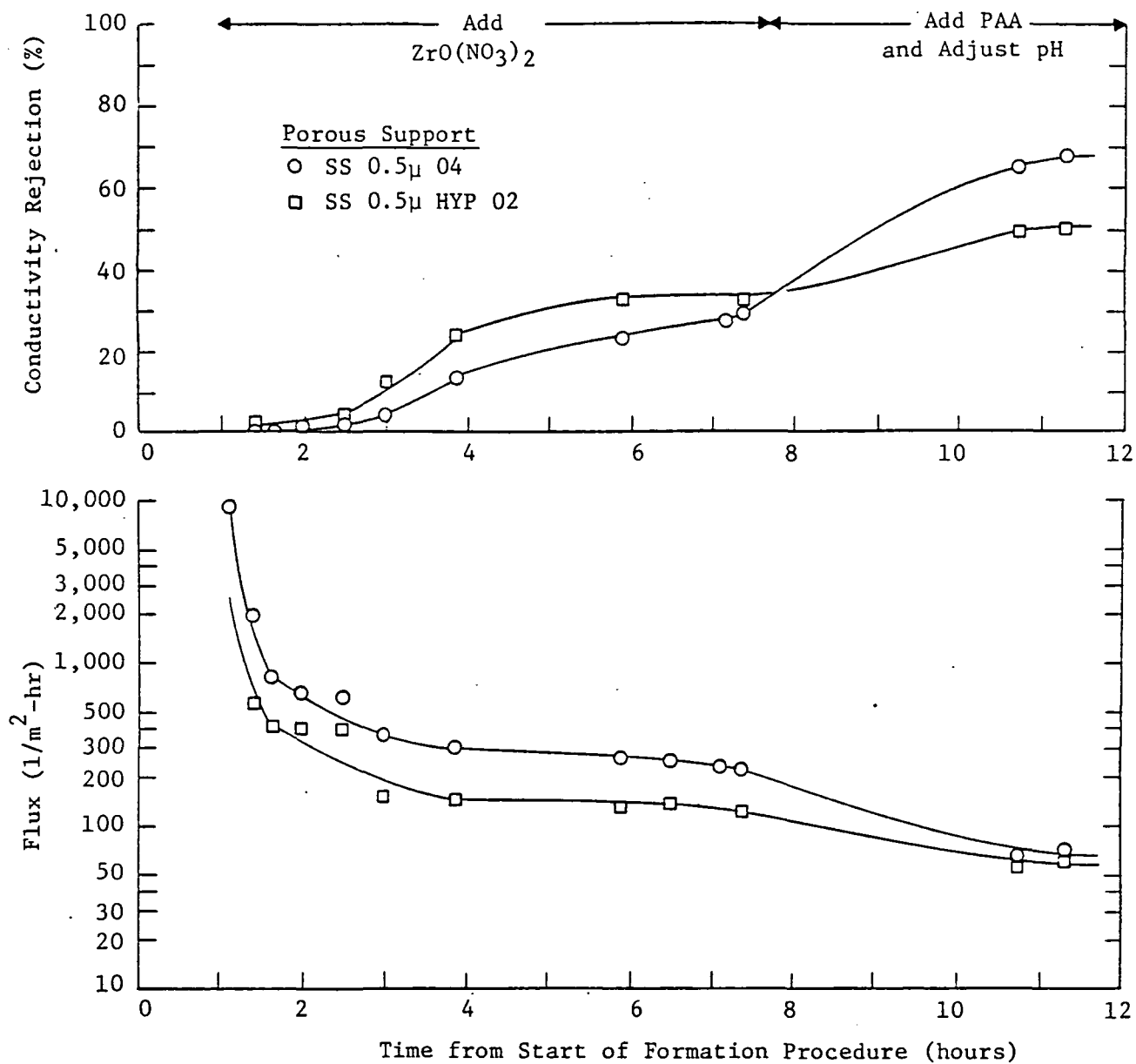


Figure 3-4 Hyperfiltration Performance vs. Time During Membrane Formation Without Carbon-Black Filteraid (0.05 M  $NaNO_3$ , 70  $kg/cm^2$ , 30°C, 4.6 mps)

These results (both rejection and flux) represented a significant advancement over the performance levels obtained previously in the program for the stainless steel supports. The ceramic supports exhibited a moderate improvement as well.

For all supports the rate of membrane formation was much more rapid than was observed in the previous formations conducted without filteraid. For example the formation time required with filteraid in Formation No. 14 was only about 5 hours, whereas over 11 hours was required when no filteraid was used in Formation No. 12. The contrast is most clearly seen by comparing Figure 3-5 to Figure 3-4.

As in the earlier runs without filteraid, no significant difference was noted between "standard" stainless steel performance and Hypertube performance when filteraid was used. Both supports exhibited rejections consistently superior to those shown by the ceramic control even though flux rates were comparable.

### 3.5 Membrane Removal Efficiency with Single Tubes

Efforts to remove the ZrO-PAA membrane from the stainless steel supports were only partially successful. Although the caustic/acid backflush technique always resulted in at least a 100-fold increase above the membrane flux level, the initial flux levels of the bare supports were not recovered. Support porosities then continued to decline with additional formation/stripping cycles.

Results for several of the stainless steel supports are shown in Figure 3-6, in which "porosity" is given in terms of the percentage of the original water flux remaining after each cycle. Of the two types of 0.5-micron support the standard type exhibited the steepest decline in porosity. After three cycles the standard support's post-cleaning water flux had been reduced to just 23% of its initial value, whereas the two Hypertube supports retained 49% and 71% of their initial values after the same number of cycles. Also, the rate of flux recovery during each cleaning procedure was significantly slower for the standard 0.5-micron tube than for the Hypertube. The entire 3-hour cleaning period was required to get maximum flux recovery for the standard tube, whereas similar recovery was achieved for the Hypertube within just 5 minutes of the start of the caustic back-flushing step.

Although the porosity of the standard 0.5-micron support exhibited a steep initial decline, it appeared to level out after three cycles to within the 15-20% range or at 22,000-29,000  $\text{l/m}^2\text{-hr}$ . As a point of reference, this flux level is considerably in excess of the 6,000-16,000  $\text{l/m}^2\text{-hr}$  level obtained for fresh ceramic supports at the same test conditions (21  $\text{kg/cm}^2$ , 20°C).

From Figure 3-6 it appears that the use of carbon-black filteraid in the membrane formation procedure may have resulted in a further loss in porosity for the Hypertube support, although additional data are needed to confirm this conclusion. It is not clear whether the use of carbon black affected the standard 0.5-micron support's porosity.

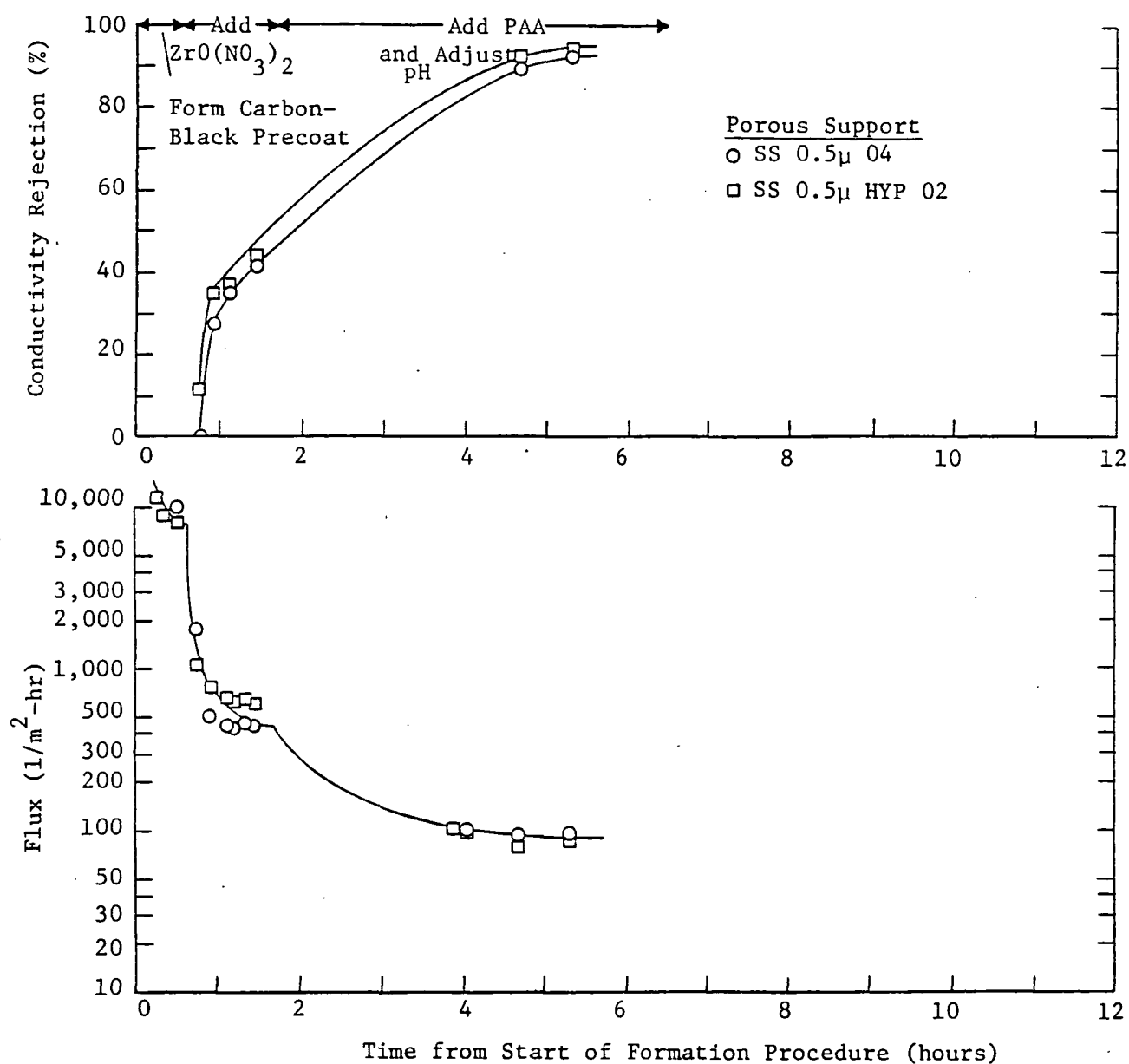


FIGURE 3-5 Hyperfiltration Performance vs. Time During Membrane Formation With Carbon-Black Filteraid (0.05 M  $\text{NaNO}_3$ , 70  $\text{kg/cm}^2$ , 30°C, 4.6 mps)

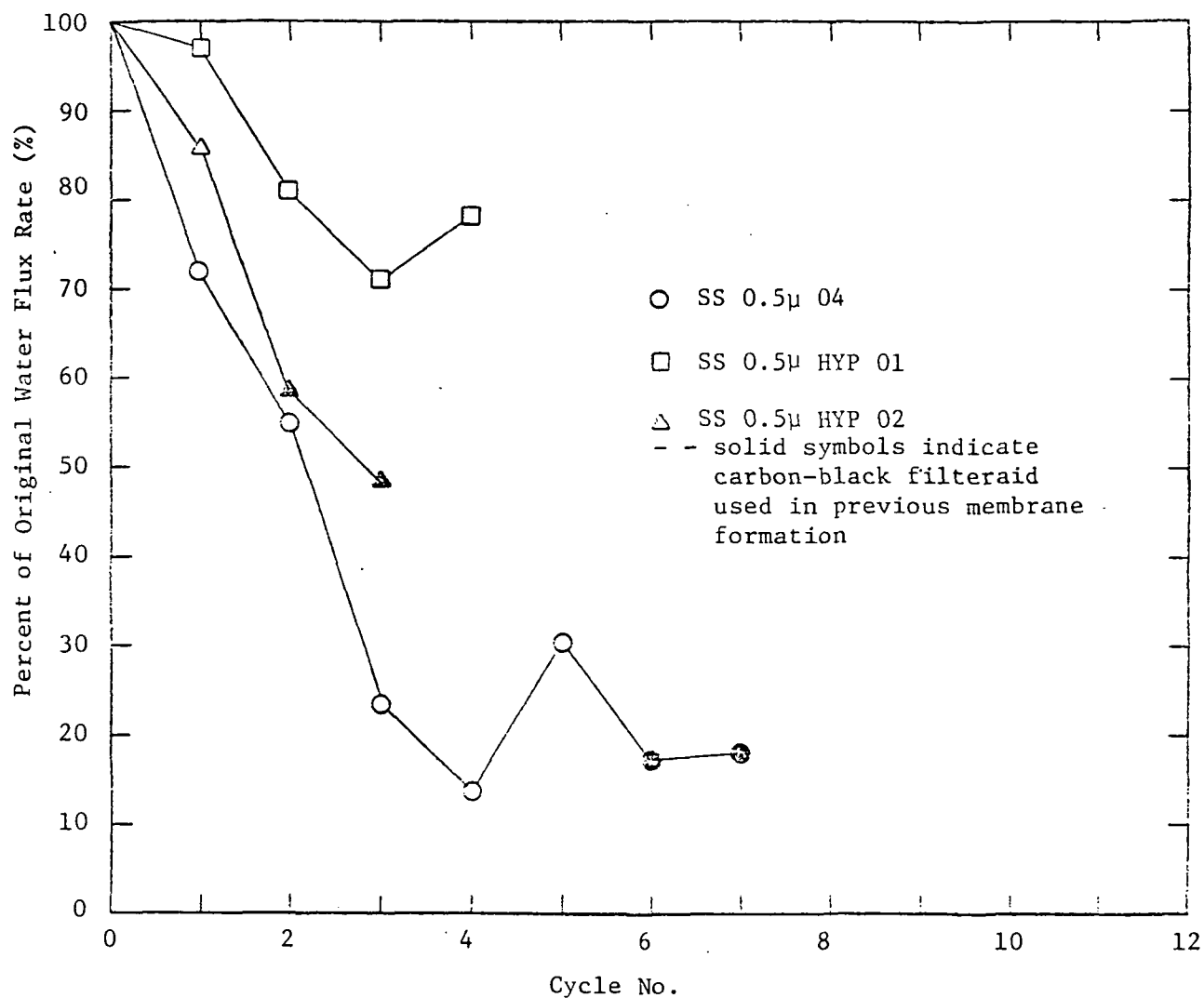


FIGURE 3-6 Porosities of Stainless Steel Supports vs. Number of Membrane Formation/Stripping Cycles

Despite the large bare-tube porosity losses suffered by the stainless steel supports after repeated usage, no correlation could be made with subsequent membrane flux performance. For example, although ZrO-PAA flux appeared to decline somewhat for two reused stainless steel supports from Formations 14 to 15 to 16, the same rate of decline was observed for the fresh ceramic controls (see Table B-2, Appendix B). This indicates that the flux decline was due to some procedural factor rather than to porosity reduction from support reuse.

As support reuse had no clear effect on membrane properties it appears possible that in situ membrane stripping and reforming could be a practical means of membrane replacement in the field. However, it should be noted that the data were obtained without interference from actual washwater process foulants, a factor which could have a significant bearing on the ability to strip and reform membranes on a repetitive basis.

### 3.6 Membrane Storage Stability with Single Tubes

At program initiation little was known about the possible effects that depressurization and subsequent storage could have on the performance of dynamically formed membranes. Clemson has acknowledged that performance of ZrO-PAA membranes is sometimes lost during storage (19), but no explicit data have been published which pertain to this important variable. Therefore, considerable emphasis was placed during this program on systematically evaluating the effects of short ( $< 24$  hours) and long (up to 500 hours) storage periods on ZrO-PAA membrane performance. In the single-tube tests, the effects of storage were determined for membranes formed both without filteraid (Table 3-7) and with filteraid (Tables 3-8 to 3-10). All hyperfiltration performance measurements were conducted under standard conditions (0.05 M  $\text{NaNO}_3$ , pH 6.8-7.2, 70 kg/cm<sup>2</sup>, 30°C, 4.6 mps).

#### 3.6.1 Stability of Membranes Formed Without Filteraid

Shutdown effects for ZrO-PAA membranes formed without filteraid were determined following Formation Nos. 01, 02, and 12. As shown in Table 3-7, each of the membranes evaluated showed significant performance declines after shutdown and subsequent startup. By far the poorest stability was exhibited by membranes formed on standard 0.5-micron stainless steel supports in Formation No. 01. These membranes suffered declines in conductivity rejection from 92% to 38-63% with large accompanying flux increases. Although the membranes had experienced a relatively long storage period (240 hours), the cause of the severe performance losses was more likely related to the use of heavily contaminated membrane formation solution, as described above. These contaminants could easily have become imbedded within the membrane matrix during the original formation and then become dislodged during the flow and pressure surges accompanying post-storage start-up. The resultant membrane defects would thus account for the observed rejection losses.

In comparison the feed solutions used in Formation Nos. 02 and 12 were less contaminated, and membrane performance stability was somewhat improved. However,

TABLE 3-7 EFFECT OF SYSTEM SHUTDOWN ON PERFORMANCE OF ZrO-PAA  
MEMBRANES FORMED WITHOUT FILTERAID (0.05 M  $\text{NaNO}_3$ ,  
70 KG/ $\text{CM}^2$ , 30°C, 4.6 MPS)

Membrane Formation No.	Length of Shutdown (hours)	Porous Support	Rejection (%)		Flux ( $\text{l/m}^2\text{-hr}$ )	
			Before Shutdown*	After Shutdown**	Before Shutdown*	After Shutdown**
01	240	SS 0.5 $\mu$ 01	92.0	62.5	64.0	99.5
		SS 0.5 $\mu$ 02	92.2	37.5	48.6	163
02	41	SS 0.5 $\mu$ 01	89.1	87.7	36.3	65.0
		SS 0.5 $\mu$ 02	91.9	87.6	46.3	49.4
		ceramic 0.3 $\mu$ 03	86.1	78.7	35.8	54.2
		ceramic 0.3 $\mu$ 04	87.5	86.2	36.7	51.3
12	16	SS 0.5 $\mu$ 04	67.9	55.4	71.5	82.9
		SS 0.5 $\mu$ HYP 02	50.0	41.2	59.8	70.1
		ceramic 0.3 $\mu$ 18	77.7	65.7	67.6	92.2

\* Measured at end of membrane formation.

\*\* Measured after 1-3 hours of continuous operation.

although the feed solution used in Formation No. 12 was the cleanest used to date (no contaminants at all were observed), rejection losses following a 16-hour shutdown period remained unacceptably high. This indicates that the ZrO-PAA membrane may be inherently unstable.

The type of support used had no clear effect on the degree of membrane instability. Rejection losses were generally comparable in any given run for the two types of material (stainless steel and ceramic) and the two stainless steel sub-types (standard 0.5-micron and Hypertube 0.5-micron).

### 3.6.2 Stability of Membranes Formed with Filteraid

As discussed previously, part of the rationale for not using filteraid in the initial membrane formation experiments was the suspicion that it could contribute to membrane instability. Therefore increased attention was given to stability testing in subsequent experiments where carbon-black filteraid was used (Formation Nos. 14-16).

The membranes formed in Formation No. 14 were subjected to a total of eight shutdown periods ranging from 15 to 112 hours. As shown in Table 3-8, each support type suffered a moderate rejection loss and flux increase after the first shutdown, but was affected relatively little by the next two shutdowns. Hyperfiltration performances during periods of continuous operation were quite stable. After the fourth shutdown the membranes were successfully regenerated with 50 ppm PAA, but two of the supports (standard 0.5-micron stainless steel and ceramic control) suffered significant performance declines after the ensuing 17-hour shutdown and a change of feed solutions. Surprisingly, these two supports exhibited a steady increase in rejection over the next 18 hours of accumulated operating time despite (1) two more shutdown periods of 16 and 112 hours, and (2) use of a 25-micron depth prefilter to prevent plugging of membrane defects by trace contaminants in the feed. The standard 0.5-micron support (SS 0.5,  $\mu$  04) showed a particularly strong rejection recovery, from 52.1% to 85.6%. Slightly different behavior was shown by the Hypertube support, which was unaffected by the first two shutdowns after the regeneration but suffered a rejection decline after the third (112-hour) shutdown from 92% to 77%. All three membranes were then successfully regenerated for the second time, but suffered slight-to-moderate rejection declines after the eighth and final shutdown period.

Similar instability was exhibited by the Formation 15 and 16 membranes. As seen in Table 3-9, the Formation 15 membranes suffered rejection declines from the 87-93% level to 70-80% after a 16-hour shutdown period, although they then appeared to recover slightly with continuous operation. The Formation 16 membranes also experienced declines after a 16-hour shutdown (see Table 3-10), followed by further declines for two of the membranes after a second, relatively brief (0.3-hour) shutdown. A PAA regeneration was then conducted, but complete rejection recovery was achieved only for the two Hypertube supports. The standard 0.5-micron stainless steel support showed only very slight improvement, while the ceramic support suffered a decided rejection loss and flux increase.



TABLE 3-8 EFFECT OF SYSTEM SHUTDOWN ON PERFORMANCE OF ZrO-PAA MEMBRANES FORMED WITH CARBON-BLACK FILTERAID: FORMATION NO. 14 (0.05 M  $\text{NaNO}_3$ , 70 KG/CM<sup>2</sup>, 30°C, 4.6 MPS)

Accumulated Operating Time (hours)	SS 0.5u 04		SS 0.5u HYP 02		Ceramic 0.3u 19	
	Rej (%)	Flux (l/m <sup>2</sup> -hr)	Rej (%)	Flux (l/m <sup>2</sup> -hr)	Rej (%)	Flux (l/m <sup>2</sup> -hr)
0.0-5.3	Form membranes.					
5.3	92.6	94.2	93.9	84.0	86.1	103
5.5	Shut down 15 hours.					
6.5	83.2	129	81.3	132	70.4	146
10.0	82.7	133	82.1	133	70.9	146
13.4	82.1	134	82.3	136	70.8	149
13.6	Shut down 17 hours.					
15.1	80.5	135	82.2	137	67.6	154
20.2	80.9	134	82.7	133	69.5	152
20.4	Shut down 63 hours.					
28.5	77.1	141	81.5	141	66.9	161
28.7	Shut down 44 hours.					
28.7-32.7	Regenerate membranes.					
32.7	95.2	83.4	92.9	80.0	86.4	97.5
32.9	Shut down 17 hours. Fill system with fresh 0.05 M $\text{NaNO}_3$ solution. Install 25-micron depth prefilter.					
34.0	52.1	164	90.6	86.1	76.3	125
39.8	65.9	121	92.4	79.6	84.9	104
40.0	Shut down 16 hours.					
41.6	68.4	118	91.6	77.9	81.9	108
47.9	72.9	108	91.9	77.9	84.2	104
48.1	Shut down 112 hours.					
49.2	81.2	104	77.1	94.1	82.3	109
51.9	85.6	99.3	81.9	89.5	83.9	108
52.3-56.8	Regenerate membranes.					
56.8	93.9	72.8	90.7	61.8	89.8	83.4
57.0	Shut down 15 hours.					
58.1	72.2	109	86.5	81.0	84.1	104
59.2	77.2	101	87.3	78.3	84.4	101

TABLE 3-9 EFFECT OF SYSTEM SHUTDOWN ON PERFORMANCE OF  
ZrO-PAA MEMBRANES FORMED WITH CARBON-BLACK  
FILTERAID: FORMATION NO. 15 (0.05 M  $\text{NaNO}_3$ ,  
70  $\text{KG}/\text{CM}^2$ , 30°C, 4.6 MPS)

Accumulated Operating Time (hours)	SS 0.5 $\mu$ 04		SS 0.5 $\mu$ HYP 02		Ceramic 0.3 $\mu$ 20	
	Rej (%)	Flux ( $\text{l}/\text{m}^2\text{-hr}$ )	Rej (%)	Flux ( $\text{l}/\text{m}^2\text{-hr}$ )	Rej (%)	Flux ( $\text{l}/\text{m}^2\text{-hr}$ )
0.0-6.0	Form membranes.					
6.0	90.3	83.4	92.8	74.2	86.8	77.8
6.2	Shut down 16 hours.					
8.2	73.2	121	79.7	112	70.4	112
11.9	75.8	118	81.5	108	74.0	109

TABLE 3-10 EFFECT OF SHUTDOWN AND STABILITY TESTS ON PERFORMANCE  
OF ZrO-PAA MEMBRANES FORMED WITH CARBON-BLACK FILTERAID:  
FORMATION NO. 16 (0.05 M NaNO<sub>3</sub>, 70 KG/CM<sup>2</sup>, 30°C, 4.6 MPS)

Accumulated Operating Time (hours)	SS 0.5μ 04		SS 0.5μ IYP 01		SS 0.5μ IYP 02		Ceramic 0.3μ 21					
	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)				
0.0-9.2	Form membranes.											
11.7	91.0	56.2	90.9	51.4	90.7	52.0	85.2	55.5				
11.9	Shut down 16 hours.											
13.2	84.0	77.6		69.1		70.1			70.6			
17.9	85.4	75.0		68.3		68.8			69.1			
35.9	85.9	72.2		66.0		66.0			66.0			
36.0	Shut down 0.3 hour.											
36.5	80.7	78.1	86.3	66.7	86.0	67.2	78.0	70.6				
36.9	Shut down 96 hours. Fill system with fresh 0.05 M NaNO <sub>3</sub> solution.											
36.9-39.9	Regenerate membranes.											
42.8	82.9	78.4	93.9	59.3	93.2	61.3	63.3	104				
43.0	Shut down. Ship SS tubes to IMSC for vibration/ultrasonics tests.* Tubes returned to Walden. Fill system with fresh 0.05 M NaNO <sub>3</sub> solution. Install 25-micron depth prefilter. (Total shutdown = 500 hours)											
43.7	45.2	177		13.7		463			54.8	128	26.0	401
45.1	51.2	155		16.4		360			60.3	110	31.5	336
47.1	58.1	136		37.0		169			69.2	94.7	36.5	284
64.6	71.5	112	54.7	118	81.1	84.7	46.7	207				
70.7	73.7	101	55.5	108	83.9	75.2	48.7	192				
88.0	75.5	94.5	59.5	98.8	85.7	71.1	50.7	175				
90.1	75.7	93.7	61.1	93.4	86.0	69.1	49.9	171				
90.6-93.6	Regenerate membranes.											
94.7	85.1	61.8	87.6	47.2	92.8	45.2	70.9	93.7				
113.2	85.3	61.8	87.5	47.9	94.5	44.5	68.8	93.7				

\* SS 0.5μ 04 subjected to shipping and handling only;  
SS 0.5μ IYP 01 subjected to sine vibration testing at 3.4 G's, 50 Hz for 5 minutes;  
SS 0.5μ IYP 02 subjected to ultrasonic cleaning for 1 minute at each end;  
Ceramic 0.3μ 21 stored at Walden as control membrane.

At this point the Formation 16 membranes were subjected to a number of additional, relatively severe tests. To test the effect of shipping and handling on ZrO-PAA membrane stability, the three stainless steel supports were sealed in their water-filled housings and shipped to LMSC. The ceramic support was stored at Walden as a control. Hypertube No. 01 was then subjected to mechanical vibration testing (3.4 G's, 50 Hz) for 5 minutes, and Hypertube 02 was placed in an ultrasonic cleaner for 1 minute. After return of the supports to Walden they were evaluated under standard conditions with a fresh feed solution and 25-micron depth prefiltration. The total elapsed time between this and the previous hyperfiltration measurement was approximately 500 hours.

As seen in Table 3-10, all four membranes suffered large rejection declines and flux increases following the 500-hour shutdown. The mechanical vibration testing appeared to cause the greatest damage, reducing the rejection of Hypertube 01 from 94% to 14%. The other three supports exhibited comparable, somewhat smaller rejection losses indicating that neither the ultrasonics nor the act of shipping and handling was more damaging to membrane performance than the act of shutdown, storage, and start-up per se. More detailed testing would have to be conducted to confirm this conclusion, however.

As in the previous stability tests, all four of the Formation 16 membranes exhibited remarkable improvement in rejection with continued operation after the 500-hour shutdown. The range of rejections improved from 14-55% to 50-86% after 47 hours of continuous running, with flux rates dropping from 128-463 l/m<sup>2</sup>-hr to 69-171 l/m<sup>2</sup>-hr. The performances appeared to level out, however, indicating that the original (pre-shutdown) values could not be recovered merely by running for a longer period of time. A PAA regeneration was therefore conducted, which succeeded in recovering most or all of the pre-shutdown rejection values.

Based on the single-tube results the following observations may be made concerning the stability of ZrO-PAA membranes formed with carbon-black filteraid:

- The membranes can exhibit significant rejection losses following system shutdown and subsequent start-up, regardless of the support type used. The extent of performance decline appears to be no worse than for membranes formed without filteraid, however.
- The act of depressurization appears to be the primary cause of the performance decline, although the size of the decline may be dependent on the length of storage time.
- Upon repressurization membrane performance is either very stable or, if adversely affected by storage, tends to improve with continued operation.
- Performance lost during storage can be recovered through regeneration with PAA.

### 3.7 Porous Support Selection

The single-tube tests indicated no clear differences between the hypertube and "standard" 0.5-micron stainless steel supports with regard to absolute membrane hyperfiltration performance or performance stability. Both support types

exhibited (1) very good rejections (at comparable flux rates) at the end of membrane formations with filteraid, and (2) moderate rejection losses due to system shutdown. The only obvious difference between the two was the relative ease with which the Hypertube membranes were stripped by caustic/acid back-flushing compared to the removal rate for membranes formed on the standard supports. For this reason the Hypertube was selected over the standard support for incorporation in the design of the multi-tube module.

### 3.8 Multi-Tube Module Pre-Treatment

Prior to membrane formation the multi-tube module was cleaned with 1 M  $\text{HNO}_3$  for one hour at  $20^\circ\text{C}$ . Maximum system pressure was limited to  $3 \text{ kg/cm}^2$  at the inlet and  $< 1 \text{ kg/cm}^2$  at the outlet due to the extremely high flux through the bare Hypertubes and the limited capacity of the Gaulin feed pump (12 lpm). The acid solution turned black during the wash, indicating that corrosion products had been removed from the porous tubing and/or the various other stainless steel module components.

Following cleaning the module was rinsed once-through with RO-treated tap water. During the rinse the module water flux was measured at approximately  $2040 \text{ l/m}^2\text{-hr}$  ( $2.8 \text{ kg/cm}^2$  inlet pressure,  $< 0.7 \text{ kg/cm}^2$  outlet pressure, 3.9 mps inlet feed velocity, 1.0 mps outlet velocity,  $25^\circ\text{C}$ ).

### 3.9 Multi-Tube Module Membrane Formation Results

Two complete membrane formation procedures and seven regeneration procedures were conducted with the multi-tube module. To minimize pressure drop the module subassemblies were connected in parallel for each formation and all but one of the regenerations. All of the Gaulin plunger pump's 12-lpm capacity was passed through the module during these tests, resulting in an inlet feed velocity of 3.9 mps for each subassembly. This velocity was slightly less than that used in the single-tube tests (4.6 mps) but was believed to be more than adequate.

#### 3.9.1 Formation No. 01

Detailed hyperfiltration results obtained during and after the first module membrane formation attempt are given in Table 3-11. The starting feed concentrations of carbon black, zirconyl nitrate, and PAA were presented previously in Table 3-4.

Because of the high module porosity and the limited pump capacity, initial operating pressures and feed velocities during the filteraid step were substantially less than those used earlier in the single-tube tests. Pressures were limited to  $3.5 \text{ kg/cm}^2$  (inlet) and  $< 0.7 \text{ kg/cm}^2$  (outlet) at feed velocities of 3.9 mps (inlet) and 1.5 mps (outlet) even after the standard 30-minute application period. These conditions compare to the 28-42  $\text{kg/cm}^2$  pressure range and 4.6 mps feed velocity used in the single-tube formations. However, addition of 40 ppm zirconyl nitrate resulted in rapid flux reduction, which in turn permitted steady increases in pressure and velocity to within acceptable ranges ( $70 \text{ kg/cm}^2$ , 2.7-3.7 mps).

TABLE 3-11 FLUX AND REJECTION PERFORMANCE OF MULTI-TUBE MODULE DURING AND AFTER FORMATION OF ZrO-PAA MEMBRANE WITH CARBON-BLACK FILTERAID AT 25°C: FORMATION NO. 01

	Accumulated Operating Time (hours)	Inlet/Outlet Pressure (kg/cm <sup>2</sup> )	Outlet Velocity (mps)	Feed Conductivity ( $\mu$ mhos)	Conductivity Rejection (%)	Flux (l/m <sup>2</sup> -hr)
water-flux measurement	0.0	2.8/<0.7	1.0	~40	--	2040
after carbon black precoat	0.5	3.5/<0.7	1.5	--	--	1550
after ZrO formation (pH 4)	7.3	72.4/68.2	3.4	4600	32.6	265
after ZrO-PAA formation (pH 7)	12.6	72.4/68.2	3.7	5300	<u>70.2</u>	<u>55.9</u>
after 258-hour shutdown and 1 hour of subsequent operation	13.8	72.4/68.2	3.6	4400	25.0	171
after 258-hour shutdown and 2½ hours of subsequent operation	15.3	72.4/68.2	3.7	4450	50.6	104
after regeneration with 50 ppm PAA	20.0	72.4/68.2	3.7	5150	<u>80.4</u>	<u>60.4</u>
after 39-hour shutdown and 1½ hours of subsequent operation	22.6	72.4/68.2	3.7	5050	47.5	107
after 39-hour shutdown and 2½ hours of subsequent operation	23.6	72.4/68.2	3.7	5100	54.9	94.2
after regeneration with 150 ppm PAA	28.5	72.4/68.2	3.7	5100	<u>77.3</u>	<u>63.7</u>

After 2.5 hours of exposure to the zirconium solution the module flux had decreased significantly but no conductivity rejection had yet been obtained. Therefore additional doses of both carbon black (8 ppm) and zirconyl nitrate (40 ppm) were introduced, which resulted in improvement of rejection to 21.1% at  $285 \text{ l/m}^2\text{-hr}$  flux. After an overnight shutdown period a final 40 ppm dose of zirconyl nitrate was introduced, and rejection improved to 32.6% at  $265 \text{ l/m}^2\text{-hr}$ . The performance of the zirconium membrane was now considered satisfactory, and the PAA step was initiated.

As shown in Table 3-11, the addition of 50 ppm PAA and the subsequent pH excursion resulted in a final ZrO-PAA membrane performance of 70.2% conductivity rejection at  $56 \text{ l/m}^2\text{-hr}$ . This rejection was considerably lower than the desired 88% minimum and the 90-94% range obtained previously with single Hypertubes. Moreover, performance deteriorated sharply after a 258-hour shutdown period (see Table 3-11). Rejection slowly recovered with continued operation, from 25.0% after one hour to 50.6% after 2.5 hours, but it did not appear that the original 70% level would be reached by additional operating time alone. Therefore a regeneration step was conducted with 50 ppm PAA, which succeeded in improving module performance to 80.4% rejection at  $60 \text{ l/m}^2\text{-hr}$ .

Following a third shutdown period (39 hours) the module performance was again found to have deteriorated. Regeneration with 150 ppm PAA then recovered most of the original rejection, but no further improvement on the peak value of 80% was obtained.

Because the module rejection appeared to be limited to a level below that predicted from single-tube performance, it was suspected that a physical defect in the module assembly could be allowing leakage of feed into the permeate stream. To determine whether weld leaks could be contributing to the low rejection, the module was tested briefly with its stainless steel housing removed, and the welds joining the U-bends and inlet/outlet ports to the porous tubing were observed. No leakage was detected over a period of one hour at 800 psig, indicating that some other factor was responsible for the poor rejection performance.

### 3.9.2 Module Membrane Removal

As further improvement in rejection performance was not expected to result from additional PAA regeneration attempts alone, it was decided that the membrane should be stripped and completely reformed under modified formation conditions. Accordingly, the system was converted to the back-flush mode and the membrane stripped by successive caustic acid washes. After the final water rinse the module was converted back to the normal (internal-flow) mode, and the water flux was determined to be about  $2200 \text{ l/m}^2\text{-hr}$  ( $2.8 \text{ kg/cm}^2\text{ in}$ ,  $<0.7 \text{ kg/cm}^2\text{ out}$ ,  $3.9 \text{ mps in}$ ,  $1.0 \text{ mps out}$ ,  $25^\circ\text{C}$ ). This figure compares favorably to the  $2040 \text{ l/m}^2\text{-hr}$  obtained under similar conditions prior to Formation No. 01, indicating that membrane removal was successful.

### 3.9.3 Formation No. 02

In Formation No. 01 an abnormally long time (12.6 hours) had been needed to form the ZrO-PAA membrane, primarily due to underestimation of the initial feed concentrations of carbon black, zirconyl nitrate, and PAA required for the module. This slow formation rate could have greatly enhanced the chances of impurities being incorporated into the membrane, which in turn could have contributed to both the low rejection and poor stability of the membrane. Therefore increased concentrations of all three feed constituents were chosen for Formation No. 02 (see Table 4) in hopes of 1) accelerating the formation rate and 2) improving membrane performance.

As shown in Table 3-12, the increased feed concentrations succeeded in achieving a much more rapid membrane formation rate but failed to improve rejection performance. Flux was reduced to  $199 \text{ l/m}^2\text{-hr}$  at  $70 \text{ kg/cm}^2$  within just one hour of the zirconium addition, whereas nearly seven hours had been required to reach the same level in the previous formation. As a result the total ZrO-PAA formation time of 5.8 hours was within the desired range. However, the rejections of both the ZrO membrane (15%) and the final ZrO-PAA membrane (54%) were uncharacteristically low.

A regeneration was conducted using the original feed solution (no extra PAA added), with each pH level held for one hour instead of the usual one-half hour. As seen in Table 3-12, the regeneration resulted in significant rejection improvement (to 72.3%) but was unsuccessful in achieving the desired 88% minimum. The module was then drained, rinsed, and stored overnight in fresh RO-treated tap water.

Following a 16.5-hour shutdown period the module was retested with a fresh  $0.05 \text{ M NaNO}_3$  feed solution. No loss in performance was incurred from the shutdown/startup cycle, an unexpected result considering the poor stability exhibited previously by the ZrO-PAA membrane in the first module membrane formation and in the single-tube tests. However, a second regeneration step conducted with 50 ppm PAA then had the undesired effect of reducing the rejection to just 57.5%.

Finally, a third regeneration was conducted using relatively large doses of both PAA (500 ppm) and zirconyl nitrate (200 ppm). This improved the module rejection to 74.7% at  $52 \text{ l/m}^2\text{-hr}$ , or to essentially the same level seen before the second regeneration.

Even though the module rejection was still less than the 88% target level, it was decided at this point to proceed with the first set of parametric and washwater evaluations. The results of these evaluations are presented in Section 3.11.



TABLE 3-12 FLUX AND REJECTION PERFORMANCE OF MULTI-TUBE MODULE DURING AND AFTER FORMATION OF ZrO-PAA MEMBRANE WITH CARBON-BLACK FILTERAID AT 25°C: FORMATION NO. 02

	Accumulated Operating Time (hours)	Inlet/Outlet Pressure (kg/cm <sup>2</sup> )	Outlet Feed Flow Velocity (mps)	Feed Conductivity ( $\mu$ mhos)	Conductivity Rejection (%)	Flux ( $l/m^2$ -hr)
water-flux measurement	0.0	2.8/<0.7	1.0	~40	--	2210
after carbon-black precoat	0.5	4.9/ 1.4	2.6	--	--	912
after ZrO formation (pH 4)	1.6	72.4/68.2	3.5	4400	14.8	199
after ZrO-PAA formation (pH 7)	5.8	72.4/68.2	3.7	5350	50.5	78.4
after regeneration with original formation solution	13.7	72.4/68.2	3.7	5200	72.3	61.3
after 16.5-hour shutdown and 1 hour of subsequent operation	14.8	72.4/68.2	3.7	4300	76.3	78.1
after regeneration with 50 ppm PAA	19.7	72.4/68.2	3.7	5300	57.5	81.2
after regeneration with 200 ppm ZrO(NO <sub>3</sub> ) <sub>2</sub> ·nH <sub>2</sub> O and 500 ppm PAA	24.9	72.4/68.2	3.7	5300	74.7	52.1

### 3.9.4 Results of Additional Regeneration Attempts

After the first set of parametric and washwater runs two additional regeneration procedures were conducted in a final effort to improve the ZrO-PAA module's rejection performance to an acceptable level. The procedures used and the resultant module performance characteristics are presented in Table 3-13.

The first regeneration was conducted with the module in series configuration using both zirconyl nitrate and PAA in the regeneration feed solution. After adjustment to pH 2 and the usual pH excursion the observed conductivity rejection had unexpectedly declined from the previous 75% level to just 59%. Correcting for conversion as described in Section 3.1 the intrinsic rejection was determined to be only slightly higher at 63%. This poor performance may have resulted from operation at relatively low velocity (2.2 mps) which was necessary to minimize pressure drop in the series configuration.

For the second regeneration the module was returned to the parallel configuration to allow operation at higher feed velocities. The entire ZrO-PAA membrane formation procedure -- including the carbon black, zirconyl nitrate, and PAA steps -- was then repeated in an effort to fill any large voids which may have been present in the module membrane. As seen in Table 3-13, the procedure resulted in recovery of the module rejection to nearly 79% at 27.5 l/m<sup>2</sup>-hr flux. Although again falling short of the target rejection of 88%, this membrane was chosen for evaluation in the second set of parametric and washwater tests (see Section 3.11 below).

### 3.10 Module Membrane Storage Stability

The poor stability shown by the Formation 01 module membrane was consistent with the single-tube results observed earlier. However, greatly improved resistance to shutdown and storage was shown by the Formation 02 membrane. Subsequent to the first PAA regeneration of this membrane, a 16.5-hour shutdown period had no effect on rejection (see Table 3-12). This good stability continued after additional regenerations during the parametric and washwater evaluations.

Results obtained before, during, and after the first set of parametric and washwater tests are shown in Table 3-14. Results obtained for the second set of tests are shown in Table 3-15. All data were obtained under standard operating conditions (0.05 M NaNO<sub>3</sub>, 25°C, pH 7, 70 kg/cm<sup>2</sup>, >1.5 mps average velocity). In both runs the module rejection stability appeared to be excellent despite a total of six shutdown periods lasting from one to eleven days, with intrinsic rejections varying only between 75 and 80%. At the same time module flux appeared to increase after each post-formation or post-regeneration shutdown period, but then seemed to level out in subsequent tests.

The good overall storage stability exhibited by the Formation 02 membrane was in marked contrast to that shown previously. The reason for the improved stability is not yet understood, but may be related to the

TABLE 3-13 RESULTS OF ATTEMPTS TO REGENERATE MODULE FOLLOWING  
SYNTHETIC WASHWATER RUN NO. 1 (0.05 M  $\text{NaNO}_3$ ,  $25^\circ\text{C}$ )

Regeneration Procedure	Flow Configuration	P avg. ( $\text{kg}/\text{cm}^2$ )	$\Delta P$ ( $\text{kg}/\text{cm}^2$ )	Average Feed Velocity (mps)	Conversion (%)	Conductivity Rejection (%)		Flux ( $\text{l}/\text{m}^2\text{-hr}$ )
						Observed	Intrinsic	
1. Add 50 ppm $\text{ZrO}(\text{NO}_3)_2 \cdot \text{nH}_2\text{O}$ and 50 ppm PAA.	series	70.3	21.1	2.2	27.8	59.1	62.9	47.9
2. Adjust pH to 2.0.								
3. Conduct standard pH excursion to pH 7.0.								
1. Add 16.5 ppm carbon black.	parallel	70.3	8.4	3.8	1.2	78.8	78.9	27.5
2. After 1/2 hour add 50 ppm $\text{ZrO}(\text{NO}_3)_2 \cdot \text{nH}_2\text{O}$ and adjust pH to 4.0.								
3. After 1/2 hour add 200 ppm PAA and adjust pH to 2.0.								
4. Conduct standard pH excursion to pH 7.0.								

TABLE 3-14 MODULE PERFORMANCE DATA OBTAINED UNDER STANDARD CONDITIONS,  
 RUN NO. 1 (0.05 M  $\text{NaNO}_3$ , 25°C, pH 7, 70  $\text{kg}/\text{cm}^2$ )

Time of Test	Flow Configuration	P avg ( $\text{kg}/\text{cm}^2$ )	$\Delta P$ ( $\text{kg}/\text{cm}^2$ )	Average Feed Velocity (mps)	Conversion (%)	Conductivity Rejection (%)		Flux ( $\text{l}/\text{m}^2\text{-hr}$ )
						Observed	Intrinsic	
at end of membrane formation	parallel	70.3	4.2	3.8	2.2	74.7	74.9	52.1
	(Shut down 11 days. Switch to series flow.)							
during parametric evaluation with 0.05 M $\text{NaNO}_3$	series	70.3	21.1	2.7	32.0	76.2	79.5	71.0
	(Shut down 19 hours. Conduct evaluation with synthetic washwater. Shut down 5 days.)							
after 5-day shutdown	series	70.3	21.1	2.7	32.2	75.8	79.1	71.3

TABLE 3-15 MODULE PERFORMANCE DATA OBTAINED UNDER STANDARD CONDITIONS,  
 RUN NO. 2 (0.05 M  $\text{NaNO}_3$ , 25°C, pH 7, 70  $\text{KG}/\text{CM}^2$ )

Time of Test	Flow Configuration	P avg ( $\text{kg}/\text{cm}^2$ )	$\Delta P$ ( $\text{kg}/\text{cm}^2$ )	Average Feed Velocity (mps)	Conversion (%)	Conductivity Rejection (%)		Flux ( $1/\text{m}^2\text{-hr}$ )
						Observed	Intrinsic	
at end of membrane regeneration	parallel	70.3	8.4	3.8	1.2	78.8	78.9	27.5
	(Shut down 19 hours. Switch to series flow.)							
during parametric evaluation with 0.05 M $\text{NaNO}_3$	series	70.3	21.1	1.6	41.5	71.4	76.4	58.4
	(Shut down 22 hours. Conduct evaluation with synthetic wastewater. Shut down 3 days.)							
after 3-day shutdown	series	70.3.	21.1	2.3	34.9	72.4	76.4	66.9

use of relatively high zirconium and PAA concentrations during formation and regeneration. However, it is recognized that even this type of membrane could be susceptible to damage from relatively severe upsets such as those expected during launch. Although no mechanical vibration tests were conducted with the Formation 02 module membrane, the results of such testing with the single tubes indicate that some module rejection loss can be expected under realistic conditions.

The potential instability of the ZrO-PAA membrane has obvious implications if the membrane is to be used in spacecraft life-support applications. Even if the minimum acceptable conductivity rejection of 88% could be achieved for the multi-tube module at the end of membrane formation, it is unlikely that this level could be maintained through extended storage, shipping and handling, or severe vibrations. Therefore, unless the membrane rapidly recovers on its own during actual wastewater processing, some other means of ensuring specification membrane performance will be required. One approach would be to design into the wastewater treatment system a separate loop for automatic PAA regeneration, to be used whenever module rejection falls below specification. However, due to power limitations this step would have to be conducted under low-velocity, series flow (instead of the preferred high-velocity, parallel flow), a procedure which has not yet been successfully demonstrated. In addition, such a procedure would add to undesirable complication to the treatment system. An alternative approach would be to eliminate shutdowns altogether by running the system under pressure 100% of the time, and recycling the permeate to the feed tank during the periods when normal (once-through) operation is not required. This approach is quite energy-intensive, however. A third, and the most ideal, approach would be to improve the inherent stability of the dynamically-formed membrane through (1) modifying the present ZrO-PAA membrane formation procedure, or (2) developing new dynamically-formed membranes and/or porous support options. Such a solution may not be possible due to inherent limitations of the dynamically-formed membrane class, but it is believed to be the only practical way to make the membrane a viable component of a spacecraft wastewater treatment system.

### 3.11 Effects of Hyperfiltration Test Parameters on Module Performance

#### 3.11.1 Parametric Run No. 1

The effects of feed velocity and pressure on the performance of the ZrO-PAA module were investigated briefly in the first parametric run. The module was evaluated in series configuration at constant temperature (25°C) using a standard feed solution (0.05 M NaNO<sub>3</sub>, pH 7). Other test conditions and the module performance data are presented in Table 3-16.

Initially conditions were fixed for a period of 2.5 hours at 42 kg/cm<sup>2</sup> average pressure, ~0.9 mps (0.30 lpm) average feed flow, and approximately 50% conversion. During this time both flux and rejection stabilized quickly, with module flux as expected at 41-42 l/m<sup>2</sup>-hr. However, the intrinsic rejection range of 57-61% was significantly less than the 75% level obtained under membrane formation conditions.



At the 2.8-hour mark the average pressure was raised from 42-70 kg/cm<sup>2</sup> while the feed velocity was kept constant. The pressure increase had the anticipated effect of a directly proportionate increase in flux to 68 l/m<sup>2</sup>-hr. As the flux increase resulted in a sizable increase in conversion (and therefore in a proportionate increase in the average feed concentration across the module), the observed rejection declined from 50.2% to 40.7%. Intrinsic rejection remained as before, however, at 59%.

At the 3.5-hour mark the average feed flow was raised to 2.71 mps (0.95 lpm) while the pressure was kept constant at 70 kg/cm<sup>2</sup>. The higher velocity had the immediate and dramatic effect of improving observed rejection to 76% and intrinsic rejection to nearly 80%. At the same time the flux increased slightly to 72 l/m<sup>2</sup>-hr.

Finally, the average pressure was lowered to 42 kg/cm<sup>2</sup> while the high feed velocity (2.4 mps) was maintained. This resulted in a reduction in flux to 42 l/m<sup>2</sup>-hr, or essentially the same as that obtained earlier at the same pressure but at lower velocity (0.9 mps). Rejection, however, was significantly improved over that obtained at the lower flow rate. These data, when combined with the results obtained at 70 kg/cm<sup>2</sup>, indicate an unexpectedly strong dependence of module rejection on feed velocity.

### 3.11.2 Parametric Run No. 2

A more detailed investigation into the effects of feed velocity on module performance was conducted in the second parametric run. Also, a temperature scan was conducted beyond the pasteurization level (74°C), and data were again gathered at both 42 and 70 kg/cm<sup>2</sup>. As in the first parametric run the module was evaluated in series configuration with 0.05 M NaNO<sub>3</sub> at pH 7.

To start the run four average feed velocities (1.6, 1.1, 0.6, and 0.3 mps) were investigated in descending order at 42 kg/cm<sup>2</sup>, after which the flow was returned to the initial value in order to determine the reversibility of the velocity effects. Associated with this velocity range was a wide range of conversions (27-96%). These ranges were selected so as to include the conditions expected for washwater testing, i.e., 0.3-0.5 mps average feed velocity and 90% conversion.

Test results for the velocity excursion are presented in Table 3-17 and plotted in Figure 3-7. Although flux remained relatively constant, it can be seen that both the observed and intrinsic rejections were severely reduced with decreasing velocity and increasing conversion. In the velocity range of interest for washwater processing (0.3-0.5 mps) the observed rejections derived from Figure 3-7 were only 15-40%. However, each type of rejection was then completely recovered upon returning the velocity and conversion to their original levels. These data indicate that the ZrO-PAA membrane may be more sensitive to high solute concentration (resulting from increased concentration polarization and increased conversion) than was previously believed. This conclusion has strong implications if washwater processing is to be conducted at both low flow and high conversion, as is currently planned.



TABLE 3-17 EFFECTS OF HYPERFILTRATION TEST PARAMETERS ON PERFORMANCE OF MODULE DURING EVALUATION WITH 0.05 M  $\text{NaNO}_3$ , RUN NO. 2 (SERIES FLOW, pH 7)

Operating Time (hours)	Feed T ( $^{\circ}\text{C}$ )	P avg (kg/cm $^2$ )	$\Delta P$ (kg/cm $^2$ )	Feed Velocity (mps)		Conversion (%)	Conductivity (umhos)			Conductivity Rejection (%)		Flux (l/m $^2$ -hr)
				In	Out		Feed	Conc	Perm	Observed	Intrinsic	
0.8	25	42.2	21.1	1.91	1.34	29.8	4200	5100	1400	66.7	70.5	39.2
1.0	25	42.2	21.1	1.86	1.32	28.2	4300	5300	1350	68.6	72.0	37.4
1.3	Reduce average feed velocity from 1.59 mps to 1.09 mps.											
1.4	25	42.2	10.5	1.36	0.82	39.5	4150	5950	1500	63.9	69.4	36.8
1.4	Reduce average feed velocity from 1.09 mps to 0.63 mps.											
1.6	25	42.2	3.5	0.89	0.37	58.3	4100	7300	2150	47.6	58.3	35.7
1.7	Reduce average feed velocity from 0.63 mps to 0.26 mps.											
1.8	25	42.2	1.4	0.50	0.02	96.3	4200	7150	3700	11.9	42.8	33.4
1.9	Raise average feed velocity from 0.26 mps to 1.60 mps.											
2.0	25	42.2	21.1	1.86	1.35	27.3	4050	5200	1250	69.1	72.4	35.0
2.1	Raise average pressure from 42.2 kg/cm $^2$ to 70.3 kg/cm $^2$ .											
2.2	25	70.3	21.1	2.05	1.20	41.5	4200	6600	1200	71.4	76.4	58.4
2.3	Initiate increase in feed temperature.											
3.2	40	70.3	21.1	2.22	1.09	50.8	4300	6900	1325	69.2	76.0	77.8
3.8	66	70.3	21.1	2.15	0.83	61.3	4100	8800	1850	54.9	65.9	90.7
4.5	81	70.3	21.1	2.53	0.63	75.2	4300	12000	2800	34.9	51.8	131.1
4.5	Reduce average pressure from 70.3 kg/cm $^2$ to 42.2 kg/cm $^2$ .											
4.7	81	42.2	21.1	2.18	0.98	54.8	4400	7700	2150	51.1	60.7	86.8
5.0	Shut down.											

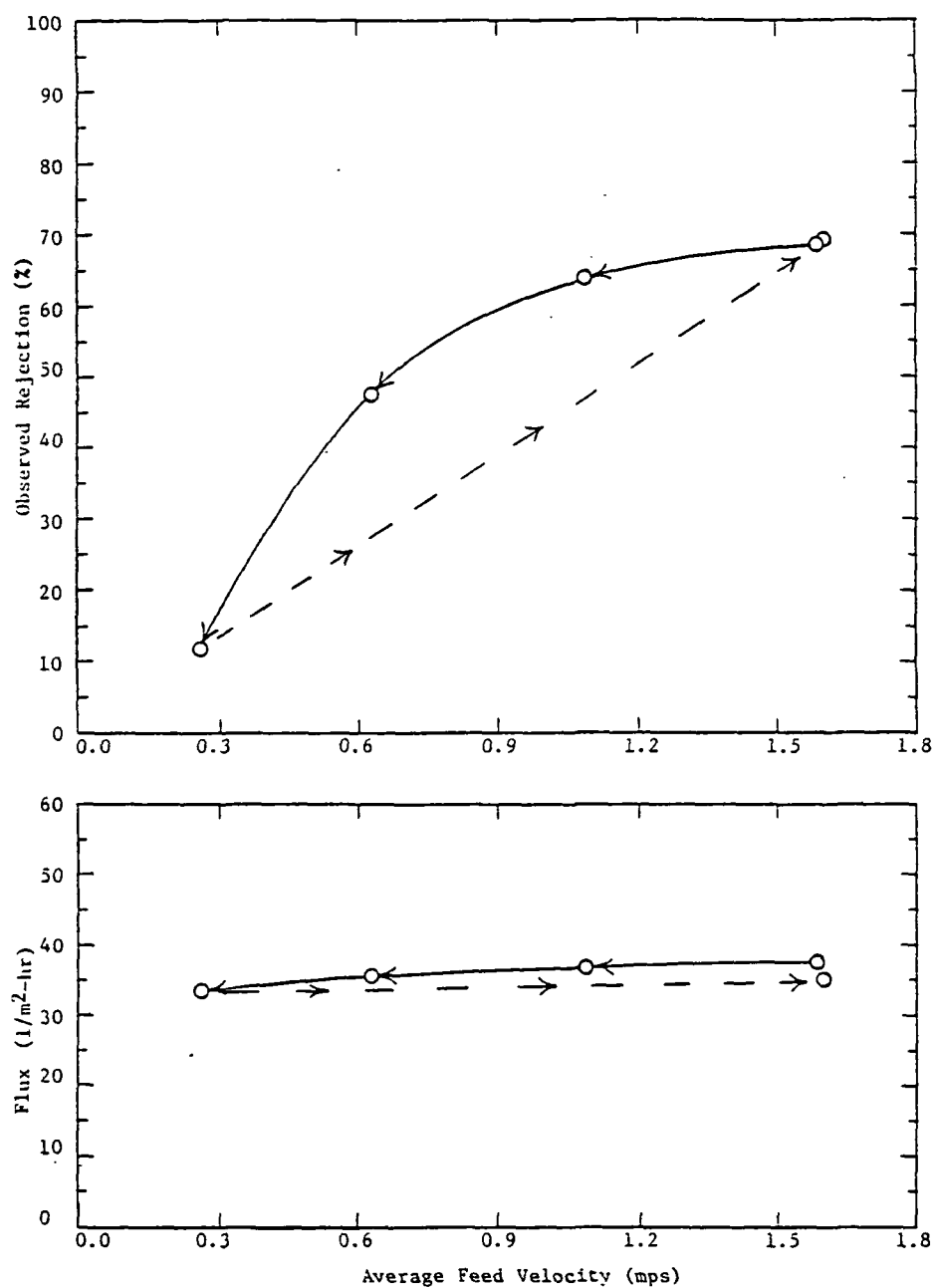


FIGURE 3-7 Effect of Feed Velocity on Module Performance (0.05 M NaNO<sub>3</sub>, 25°C, 42 kg/cm<sup>2</sup>)

After 2.1 hours of operation the average pressure was raised from 42 to 70 kg/cm<sup>2</sup> while maintaining the average feed velocity at 1.6 mps (0.57 lpm). As in the first parametric run the flux increased in direct proportion to the size of the pressure increase. However, unlike the previous run the rejection also increased even though conversion had risen from 27 to 42%.

After 2.3 hours the module performance was monitored as the feed temperature was slowly increased from 25 to 81°C. Average pressure and feed velocity were maintained approximately constant during this time. The effects of the temperature increase are shown in Table 3-17 and also plotted in Figure 3-8. As expected, the module flux increased at a rate close to the rate of reduction in water viscosity. However, the observed conductivity rejection declined from 71% at 25°C to only 35% at 81°C, while intrinsic rejection declined from 76% to 52% over the same range. These rejection losses were probably due indirectly to the parallel flux increases which occurred. As the flux increased from 58 to 131 l/m<sup>2</sup>-hr, the conversion necessarily also increased from 42 to 75%, thereby increasing the average feed concentration to a significant degree. This concentration increase apparently had an unexpectedly adverse effect on the intrinsic rejection and, therefore, on the observed rejection as well.

The final step was to return the average pressure to 42 kg/cm<sup>2</sup> while maintaining the temperature at 81°C and the average feed velocity at 1.6 mps. With the resultant flux reduction the conversion was decreased, and both the observed and intrinsic rejections were increased somewhat over those obtained at 70 kg/cm<sup>2</sup>. However, the rejections observed at 42 kg/cm<sup>2</sup> and 81°C were noticeably less than those obtained earlier at 42 kg/cm<sup>2</sup>. Again, this was probably indirectly due to the different flux rates obtained at the two temperatures.

In summary, it appears that the ZrO-PAA module will exhibit intrinsic rejections substantially less than that obtained at membrane formation (in this case ~ 75%) whenever conditions are such that relatively high solute concentrations exist at the membrane surface. These conditions include the following:

1. High Conversion (> 40%)
2. Low Average Feed Velocity (< 1 mps)
3. High Inlet Feed Concentration
4. High Membrane Flux (> 50 l/m<sup>2</sup>-hr)  
(Encouraged by high pressure and high temperature operation)

Unfortunately, the first two conditions will almost certainly exist during operation of the multi-tube module in the preprototype wastewater recovery system. To minimize the load on the permeate treatment system it is currently planned to operate the module at 90% conversion, with inlet and outlet feed flow rates of 0.19 lpm and 0.019 lpm, respectively. Based on the average feed flow rate of 0.11 lpm and the average tube diameter of 2.7 mm, the average feed velocity

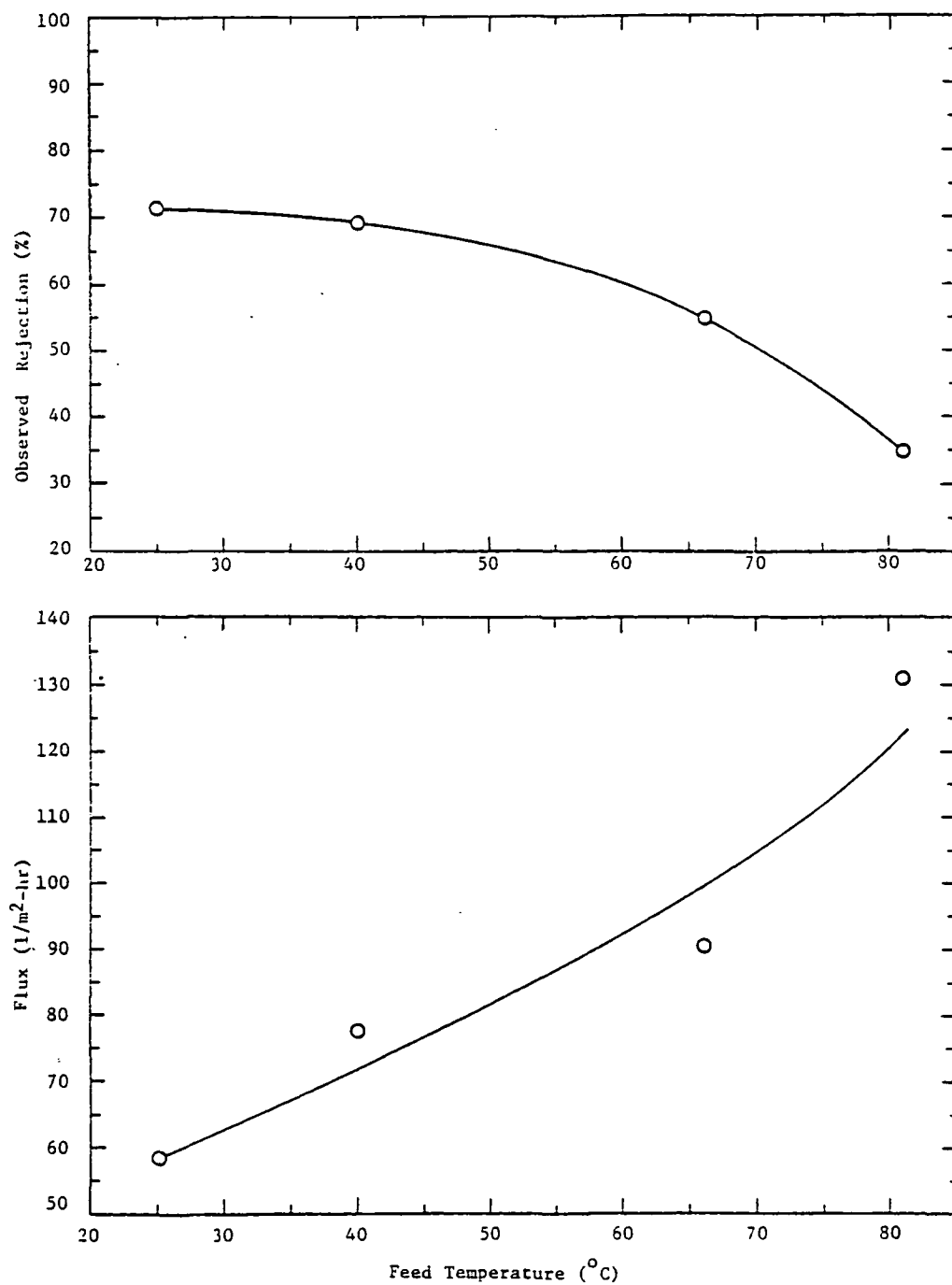


FIGURE 3-8 Effect of Feed Temperature on Module Performance (0.05 M  $\text{NaNO}_3$ , 70  $\text{kg/cm}^2$ , 5 fps) .

will be only 0.3 mps. The third and fourth conditions will not pertain as (1) the total feed solids concentration should be significantly less than the level used in the parametric tests, and (2) permeate flow is to be fixed at just 0.17 lpm or 33 l/m<sup>2</sup>hr. Overall, however, intrinsic rejection characteristics are likely to be substantially inferior to those obtainable under more ideal (high-velocity, low-conversion) conditions. Further evidence for this conclusion was obtained during brief synthetic washwater processing experiments, the results of which are presented in Section 3.12.

### 3.12 Results of Synthetic Washwater Process Tests

#### 3.12.1 Washwater Run No. 1

The first synthetic washwater run was hampered by flow-control difficulties which necessitated termination of the run after only 3 hours of operating time. However, hourly flux and conductivity-rejection values were recorded during this time and are presented in Table 3-18. Other than conductivity measurements no sample analyses were performed during this run.

All data were obtained with the module in series configuration at 90% conversion, 81°C, and 42 kg/cm<sup>2</sup> average pressure. To obtain the necessary conversion the module feed velocities were set at approximately 1.7 mps (inlet), and 0.93 mps (average). These velocities corresponded to flow rates of 0.61, 0.061, and 0.34 lpm, respectively.

As shown in Table 3-18 the module flux rate was high and stable during the 3-hour run at 105-108 l/m<sup>2</sup>-hr. Total permeate flow was 781-804 lpd, or well in excess of the target minimum of 273 lpd. However, conductivity rejections were both low and erratic. After one hour of processing the observed and intrinsic rejections were only 55% and 77%, respectively, or significantly less than the 73% observed and 88% intrinsic rejections considered acceptable for a fresh ZrO-PAA module (20). Rejections then declined to an even lower level following a 2-hour shutdown period. This decline would indicate that the membrane was damaged by the pressure cycle, but subsequent evaluation under standard conditions indicated that no permanent damage had been incurred (see Table 3-14).

After 3.3 hours of operation the run was terminated in order to investigate the cause for a rapid, steady decline in the concentrate (outlet) flow rate. Although the flow was recoverable by manual adjustment of the outlet needle valve, when left unattended the flow declined from the desired level of 60 cc/min to less than 5 cc/min in less than one-half hour. As a result it was not possible to prevent the conversion from rising beyond 90% unless the flow was kept under constant manual control.

On the assumption that some feed contaminant was passing the 440-micron strainer used to prefilter the washwater feed and subsequently fouling the flow-control valve, a number of steps were taken after the washwater run in an effort to eliminate the foulant. A 60-micron filter was installed just upstream of the valve in an effort to protect the valve from being fouled, but in subsequent operation the concentrate flow continued to rapidly decline. Replacement of the needle valve and cleaning of

TABLE 3-18 FLUX AND CONDUCTIVITY-REJECTION RESULTS OBTAINED DURING SYNTHETIC WASHWATER  
 RUN NO. 1 (SERIES FLOW, 90% CONVERSION, 81°C, 42 KG/CM<sup>2</sup>, ΔP 2.8-4.2 KG/CM<sup>2</sup>)

Operating Time (hours)	Feed Velocity (mps)			Conversion (%)	Conductivity (μmhos)			Feed pH	Conductivity Rejection (%)		Flux (l/m <sup>2</sup> -hr)
	In	Out	Avg		Feed	Conc	Perm		Observed	Intrinsic	
1.0	1.69	0.17	0.93	89.9	700	3050	315	8.6	55.0	77.4	105
1.1	Shut down ~ 2 hours.										
2.1	1.74	0.17	0.96	90.2	720	4000	580	--	19.4	44.1	108
3.1	1.73	0.17	0.95	90.1	710	4000	540	--	23.9	50.0	107
3.3	Shut down.										

of the flow meter also had no effect. To determine whether the washwater constituents and/or high-temperature operation could be affecting the fouling rate, the washwater feed was replaced with fresh RO-treated tap water and the system operated at ambient temperature. These steps appeared to eliminate the flow decline. After increasing the feed temperature to 81°C the flow still appeared to be much steadier; however, after overnight operation the flow had again been reduced to less than 5 cc/min.

The cause for the flow-control difficulties during washwater testing is not yet understood. It is possible, though, that the valve was being fouled by excess membrane formation constituents present in the system despite extensive rinsing. For example, on several occasions a discharge of carbon-black filteraid was observed passing the concentrate flow meter immediately after system startup. The presence of excess PAA in the system was also confirmed in later tests (described below). These constituents could eventually have been purged from the module and system with sufficient operating time, which in turn may have eliminated the flow-control problem. However, due to scheduling limitations it was necessary to tolerate the problem in the short run and proceed with the second washwater evaluation despite the poor flow control.

### 3.12.2 Wash Water Run No. 2

The second synthetic washwater run was conducted for the desired 50-hour period with little difficulty. Although the concentrate flow continued to decline when left unattended (resulting in conversions as high as 99%), during performance readings and sample withdrawal the flow was manually controlled at the level required for 90% conversion. The only unusual event occurred at the 21.5-hour mark when the outlet pressure suddenly began to decline while the inlet pressure remained constant at 42 kg/cm<sup>2</sup>. When the outlet pressure reached 0 kg/cm<sup>2</sup> a significant mass of viscous PAA gel was expelled by the large pressure drop through the needle valve, flow meter, and concentrate sample valve, which was fortunately being used at the time. The outlet pressure then returned to its former level of 39 kg/cm<sup>2</sup>. Apparently, excess PAA gel previously deposited on the inside surfaces of the module tubing had been loosened by the high operating temperature and eventually resulted in plugging the flow path. Further gel generation was not observed for the remainder of the test.

Flux and conductivity-rejection data are presented in Table 3-19 and plotted in Figure 3-9. As in the first wash water run the module flux was both high (generally 85-94 l/m<sup>2</sup>-hr) and remarkably stable. However, conductivity rejections were again very low and extremely erratic. The maximum observed conductivity rejection was only 50% (75% intrinsic), and many readings were only 0% even though significant feed concentration had obviously occurred (see Table 3-19).

Feed, concentrate, and permeate samples were withdrawn for analysis after 1 and 50 hours of operation, with results presented in Table 3-20. As with conductivity rejection, the rejections of the other key washwater components were generally both low and erratic. Observed ammonia rejection was at 0% after 1 hour but then appeared to improve substantially (to 35%)

TABLE 3-19 FLUX AND CONDUCTIVITY-REJECTION RESULTS OBTAINED DURING SYNTHETIC WASHWATER  
RUN NO.2 (SERIES FLOW, 90% MINIMUM CONVERSION, 81°C, 42 KG/CM<sup>2</sup>, ΔP 2.8-3.5 KG/CM<sup>2</sup>)

Operating Time (hours)	Feed Velocity (mps)		Avg	Conversion (%)	Conductivity (umhos)			Feed pH	Conductivity Rejection (%)		Flux (l/m <sup>2</sup> -hr)
	In	Out			Feed	Conc	Perm		Observed	Intrinsic	
0.1	1.22	0.11	0.67	90.7	--	--	--	--	--	--	76.2
1.0	--	0.11	--	--	620	7200	430	8.4	30.6	59.1*	--
2.0	1.48	0.11	0.80	92.3	630	6300	470	8.6	25.4	54.5	94.2
3.0	1.40	0.11	0.76	91.8	635	5000	710	--	0.0	0.0	88.3
21.4	Concentrate flow reduced to <0.02 mps (ΔP = 10.5 kg/cm <sup>2</sup> ). Reset concentrate flow to 0.11 mps (ΔP = 2.8 kg/cm <sup>2</sup> ).										
22.0	1.40	0.11	0.76	91.8	600	4900	300	8.5	50.0	75.4	88.3
23.0	1.36	0.11	0.74	91.6	600	6200	475	--	20.8	47.8	85.9
24.0	1.36	0.11	0.74	91.6	605	6100	590	--	2.4	9.4	85.9
25.0	1.43	0.11	0.77	92.0	610	7200	540	--	11.5	33.4	90.7
26.0	1.38	0.11	0.75	91.7	625	5600	600	8.4	4.0	14.7	87.1
27.0	1.36	0.11	0.74	91.6	625	5900	640	8.4	0.0	0.0	85.9
42.5	Concentrate flow reduced to <0.02 mps (ΔP = 6.3 kg/cm <sup>2</sup> ). Reset concentrate flow to 0.11 mps (ΔP = 2.8 kg/cm <sup>2</sup> ).										
43.0	1.40	0.11	0.76	91.8	580	11750	580	8.8	0.0	0.0	88.3
44.0	1.41	0.11	0.76	91.9	565	12100	595	8.8	0.0	0.0	89.5
45.0	1.38	0.11	0.75	91.7	600	12500	530	8.9	11.7	33.3	87.1
46.0	1.40	0.11	0.76	91.8	600	7600	525	8.9	12.5	35.0	88.3
47.0	1.45	0.11	0.78	92.2	605	5800	605	8.8	0.0	0.0	92.4
48.0	1.31	0.11	0.71	91.3	605	5000	605	8.8	0.0	0.0	82.5
49.0	1.41	0.11	0.76	91.9	610	5700	470	8.7	23.0	51.1	89.5
50.0	1.36	0.11	0.74	91.6	600	3900	595	--	0.8	3.4	85.9
50.5	Shut down.										

\* Assumes 91.5% conversion.



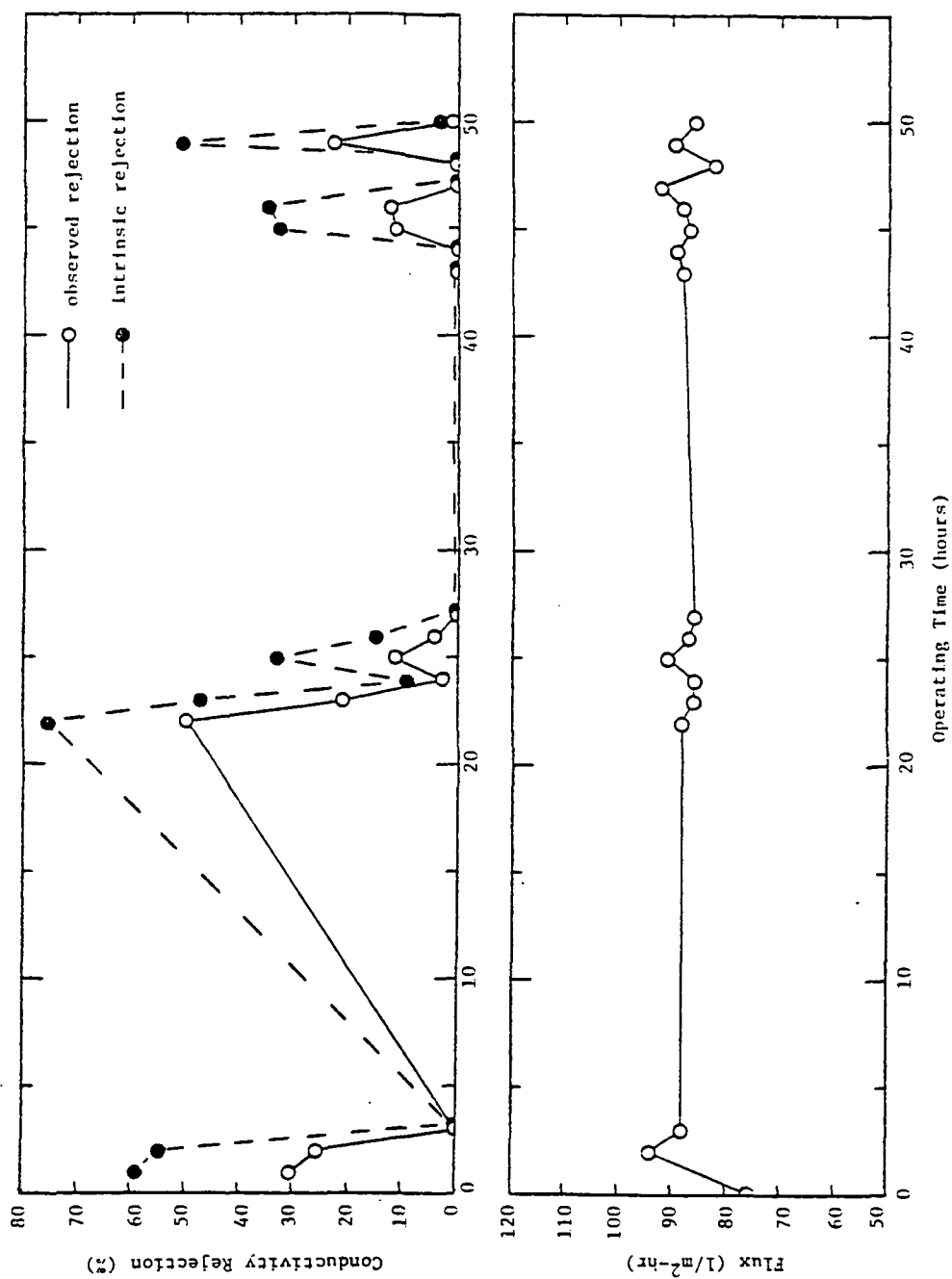


FIGURE 3-9 Flux and Conductivity-Rejection Results Obtained During Synthetic Washwater Run No. 2 (Series Flow, 90% Minimum Conversion, 81°C, 42 kg/cm²)

TABLE 3-20 ANALYTICAL RESULTS FOR SAMPLES TAKEN AFTER 1 AND 50 HOURS DURING SYNTHETIC WASHWATER RUN NO. 2

Constituent	Time of Sample Withdrawal (hours)	Concentration		Rejection (%)	
		Feed	Perm	Observed	Intrinsic
ammonia (mg/l)	1	18	180	18	0.0
	50	17	136	11	63.6
urea (mg/l)	1	60	103	56	22.0
	50	39	60	28	56.6
total organic carbon (mg/l)	1	197	4,110	57	87.5
	50	86	1,700	90	0.0
total solids (mg/l)	1	774	12,100	444	69.8
	50	482	5,340	264	71.8
conductivity (µmhos)	1	620	7,200	430	59.1
	50	600	3,900	595	3.4
turbidity (NTU)	1	32	700	14	79.3
	50	36	240	0.76	99.2

by the 50-hour mark. Urea rejection behaved similarly, increasing from 7% to 28%. However, the reverse trend was true for total organic carbon (TOC) rejections. The observed TOC rejection at the 1-hour mark was acceptably high at 71%, but, as with the conductivity rejection, appeared to have declined sharply by the end of the run. The most stable rejections were exhibited for total solids (43-45% observed, 70-72% intrinsic) and turbidity (56-98% observed, 79-99% intrinsic).

Throughout the run the feed samples were observed to be slightly turbid, while the concentrate samples were opaque (white) in appearance. The permeate samples were quite clear but foamed slightly when agitated.

As seen in Table 3-20, significant declines in the urea, TOC, and total solids feed concentrations were observed. The urea loss was most likely due to decomposition to ammonia, although a proportionate increase in the ammonia concentration was not observed (probably due to evaporation). The cause of the TOC and total solids losses is not known, although it is conceivable that they were at least partially due to adsorption by excess carbon filteraid present in the module and test loop.

The rejections of conductivity, TOC, ammonia, and urea were significantly less than those considered acceptable for wastewater processing (20). This was partially due to the relatively low intrinsic salt rejection (~75%) obtained for the module membrane, while further losses were undoubtedly caused by the combined effects of low-velocity, high-conversion, and high-flux operation. These effects might not be so severe for module membranes having higher intrinsic rejection capability. Also, it is possible that improved rejections would be obtained during processing of actual wastewater due to plugging of membrane defects by colloids not present in synthetic feeds. Both hypotheses remain to be demonstrated, however.

The reason for the wide fluctuation in solute rejection levels is not yet understood. Such erratic performance contrasts sharply with the excellent rejection stability exhibited by the module in tests with sodium nitrate under standard conditions (see Table 3-13).

### 3.13 Feed Pump Development

The first pump to be tested was a special gear pump designed and built by PDI. It, however, consumed 430 watts, rather than the specified maximum of 100 watts. This was due to problems with the leakage of water through the pump clearances. It was not possible to improve this performance with this pump concept. Therefore, alternates were explored.

A commercial pump was tested for power consumption. Average power into the pump gearbox (not motor) was 87.1 watts at 750 psi and 0.05 GPM, and 102.1 watts at 1000 psi. These power numbers were with the commercial worm type gearbox.

The pump was modified by replacing the existing motor with a 400 Hz 3 phase motor, and the existing gear box with one with the proper gear ratio. Spur gear reducers were used because they have higher efficiencies than worm gear reducers.

Two pumps were assembled and one was subjected to life testing. Preliminary performance figures indicated an average power of 60 watts at 650 psi and 85 watts at 1050 psi. This is an average power of 72.5 watts at the average system operating pressure of 850 psi. The flow rate was  $0.05 \pm .004$  GPM over the total pressure range. At the completion of the life test, both pumps were acceptance tested.

The acceptance test of the pumps were successfully completed. The pumps were disassembled and inspected, and no gear wear or other damage was apparent. As the pumps were run, the power increased slightly, evidently due to seating of the packings. The power on these units stabilized at 100 watts at 1050 psi and 75 watts at 650 psi at a 0.057 gpm average flow rate. This would result in approximately 80 watts average power at the average system conditions of 850 psi and 0.05 gpm.

### 3.14 Urea/Ammonia Removal Unit

Tests to remove urea with NaOCl were conducted. Concentrations of 1.2, 1.6 and 2.0 times the stoichiometric amount were tried. As shown in Figure 3-10, the amount of NaOCl determines the end point of the reaction. Figure 3-11 presents the final concentration ratio versus the amount of NaOCl. From these data, if the inlet urea concentration is 43 PPM (about 20 mg/l TKN) then 1.8 times the stoichiometric amount of NaOCl is required to reduce the outlet value to less than 5 PPM.

Since residual NaOCl in the permeate is undesirable, catalyst to decompose any excess NaOCl were evaluated in the apparatus shown in Figure 3-12. Cobalt oxide catalyst provided a reduction in NaOCl level but was not stable in a water solution. Therefore, other catalysts were tried. Platinum and nickel catalysts on an alumina substrate were tried. Neither provided adequate reduction as indicated in Figure 3-13.

Because metal catalysts did not properly remove NaOCl, carbon was utilized. Carbon both adsorbs NaOCl and causes a reaction which decomposes it. Using commercial data, a carbon bed was sized for 180 days of operation with an inlet of 300 ppm of NaOCl (twice the stoichiometric amount) and an outlet of less than 0.01 PPM. The resulting bed is about 3 inches in diameter and 12 inches long.

A full-scale bed was built and tested at flowrates ranging from 0.17 to 1.55 times the nominal flow. With 300 PPM of NaOCl at the inlet, there was no NaOCl detectable at the outlet (less than 1 PPM).

### 3.15 Pressure Control Module

Possible problems envisioned for the viscojet were erosion from cavitation of the hot liquid, and clogging due to dissolved solids. Therefore, as shown in Figure 3-14, a test rig was set up to allow a viscojet life test.

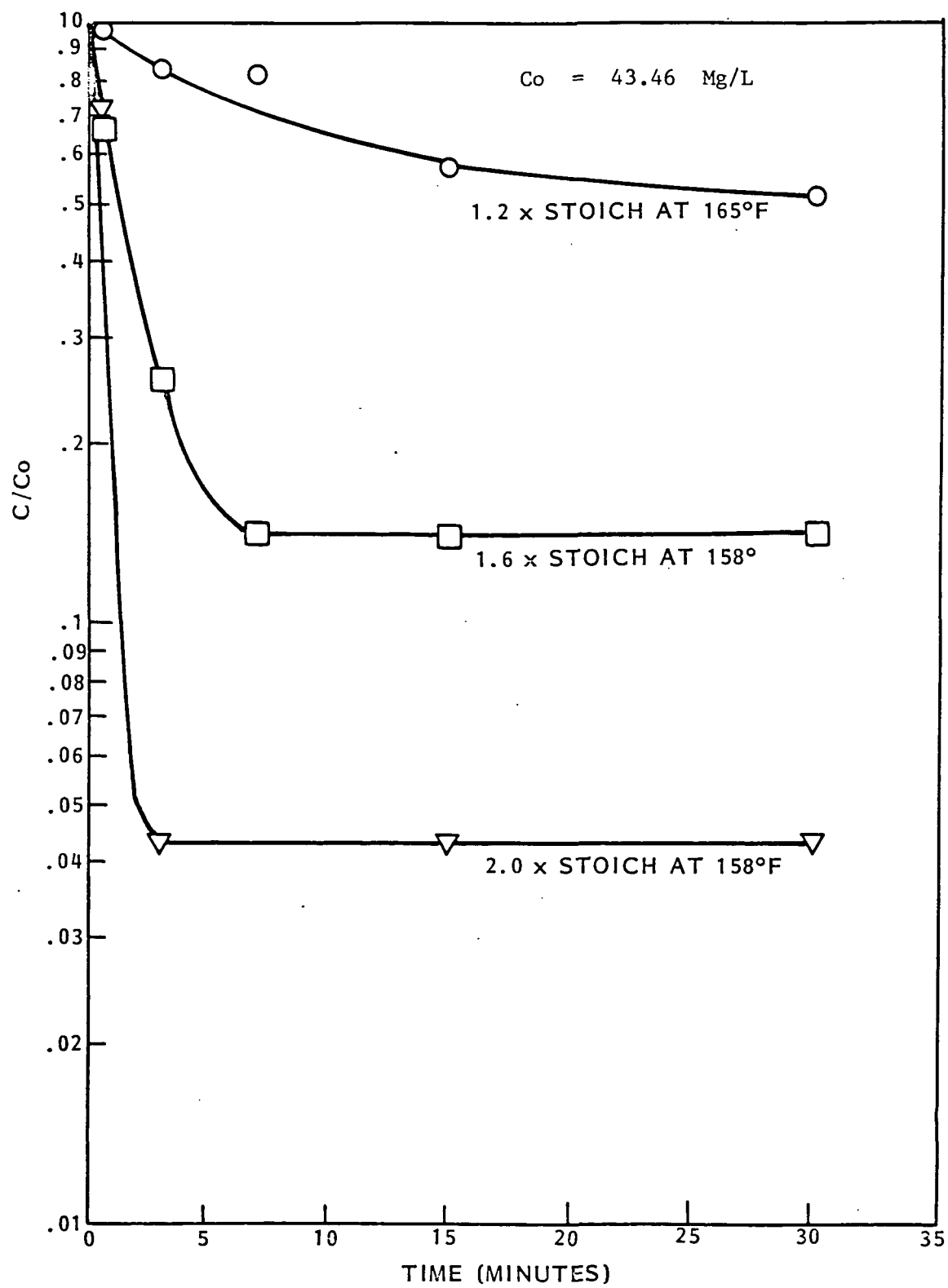
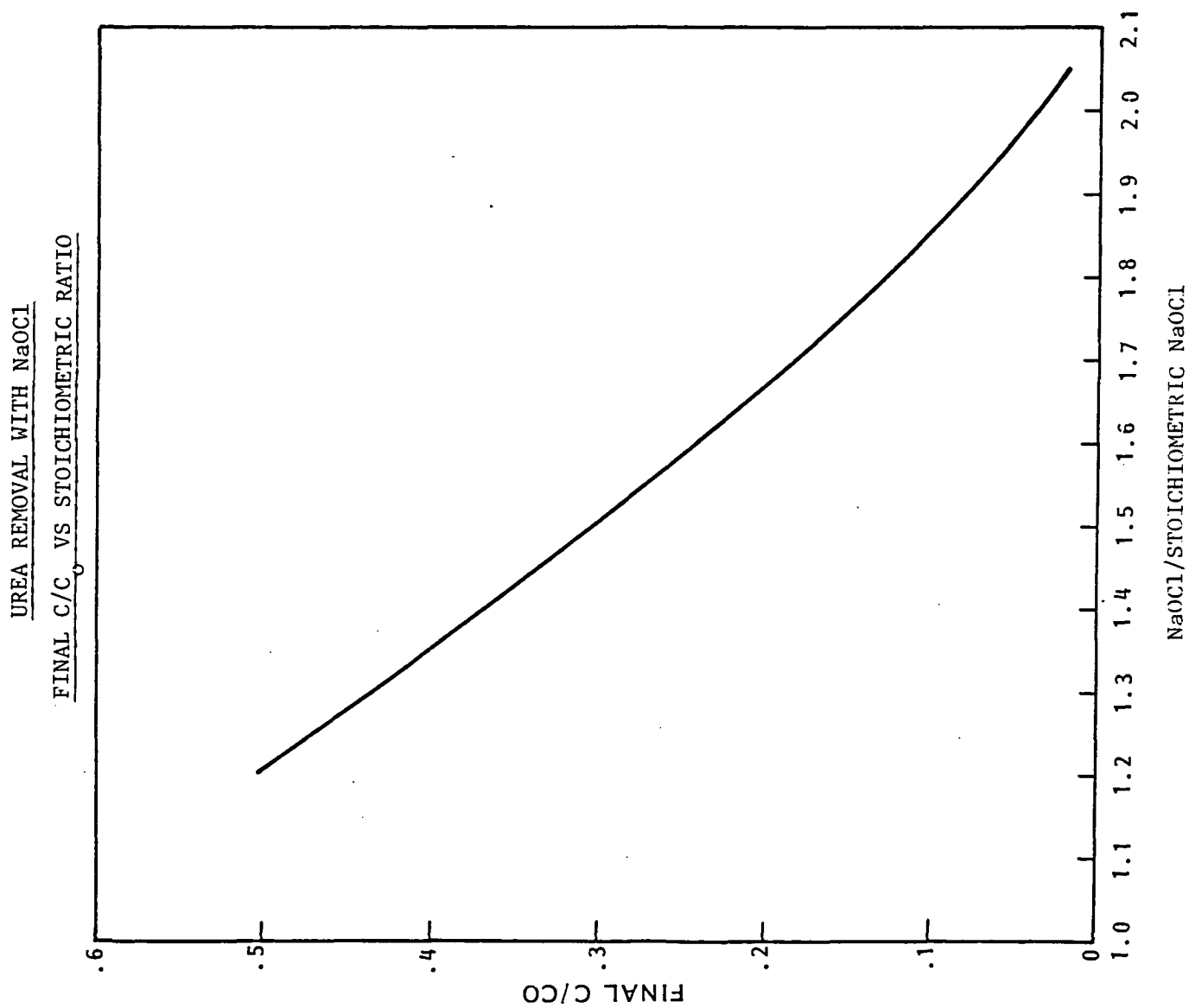


FIGURE 3-10

UREA REMOVAL WITH NaOCl

FIGURE 3-11



2-2

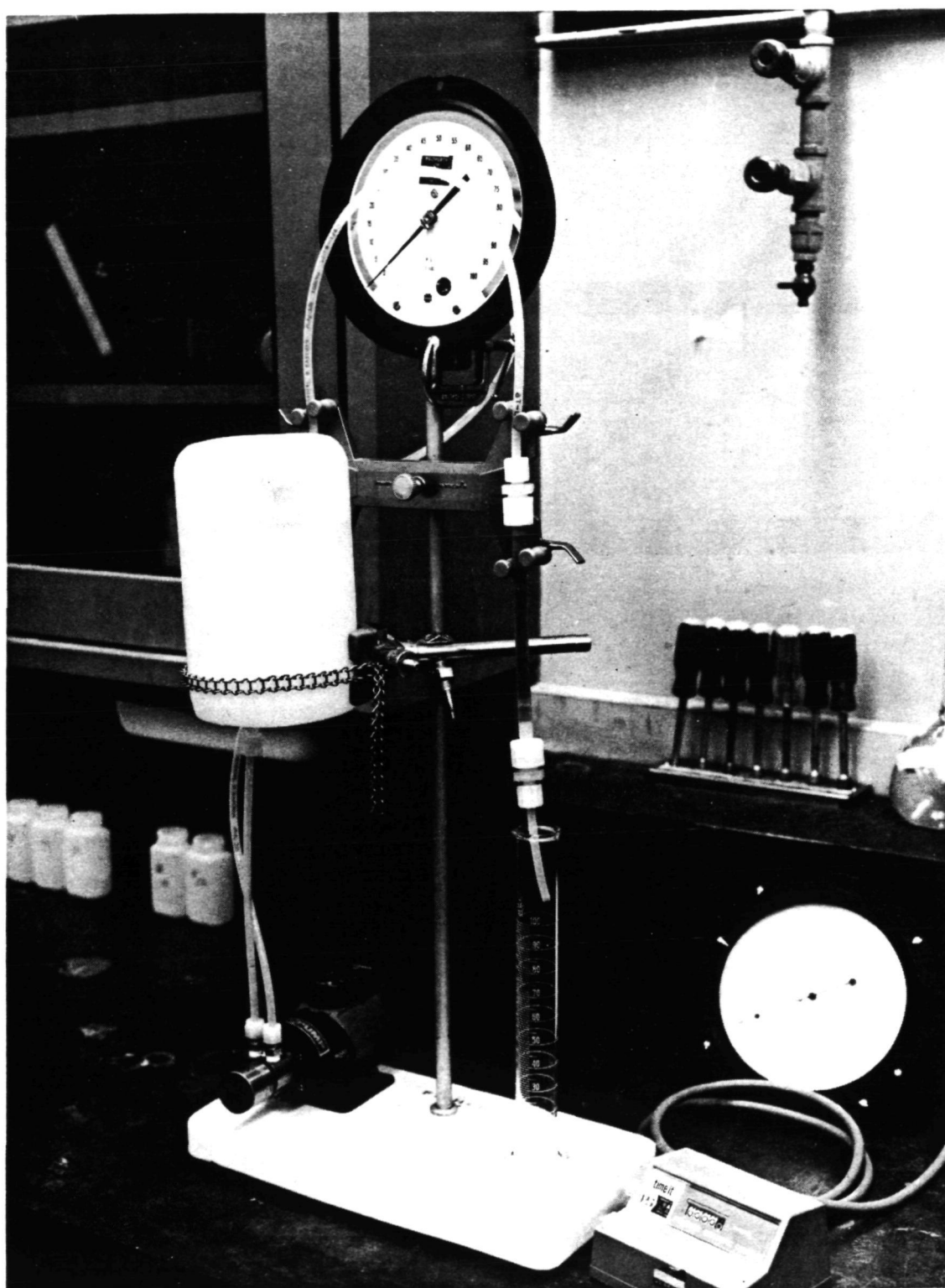


FIGURE 3-12 APPARATUS FOR EVALUATING NaOCl CATALYTIC DECOMPOSITION

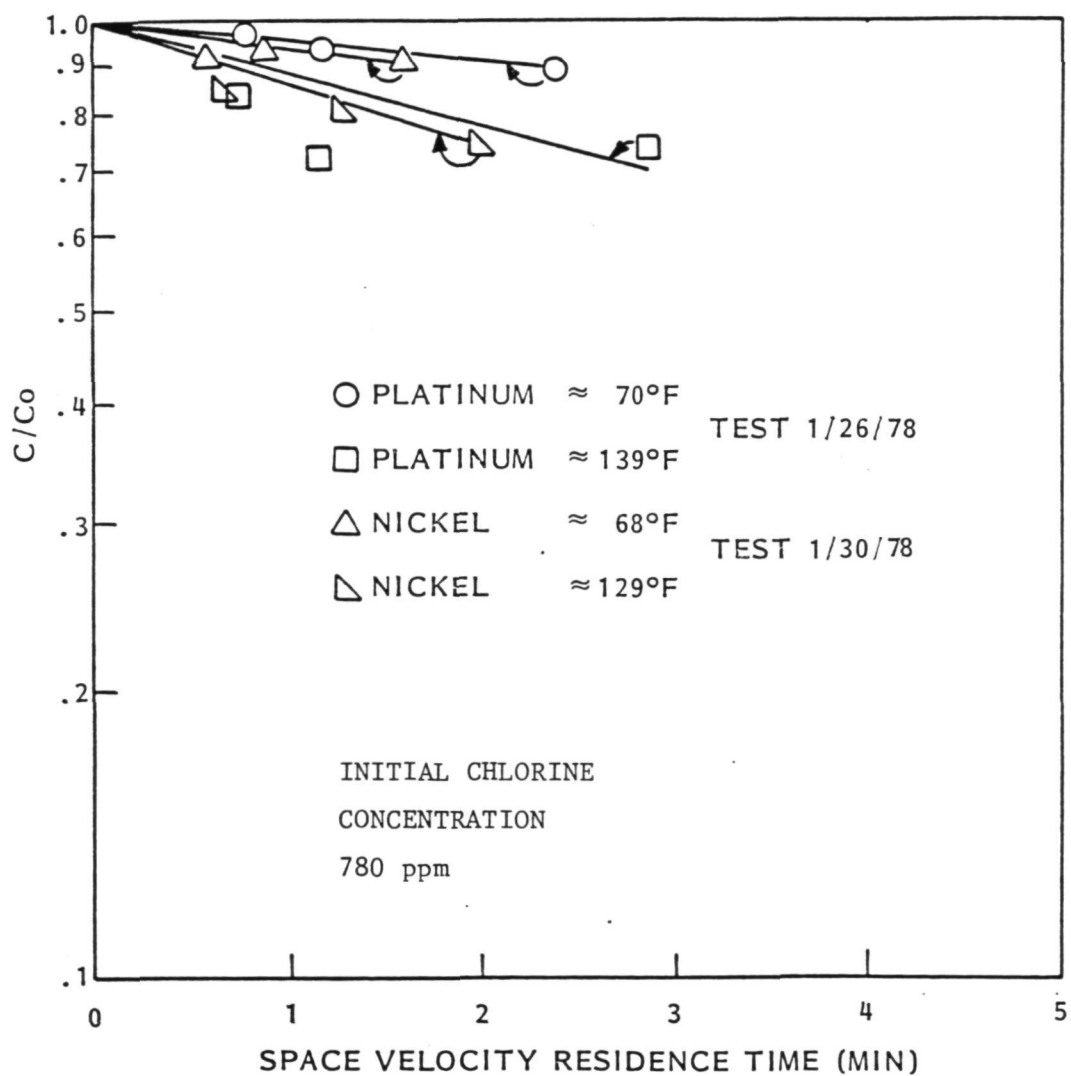


FIGURE 3-13

NaOCl REDUCTION USING CATALYST



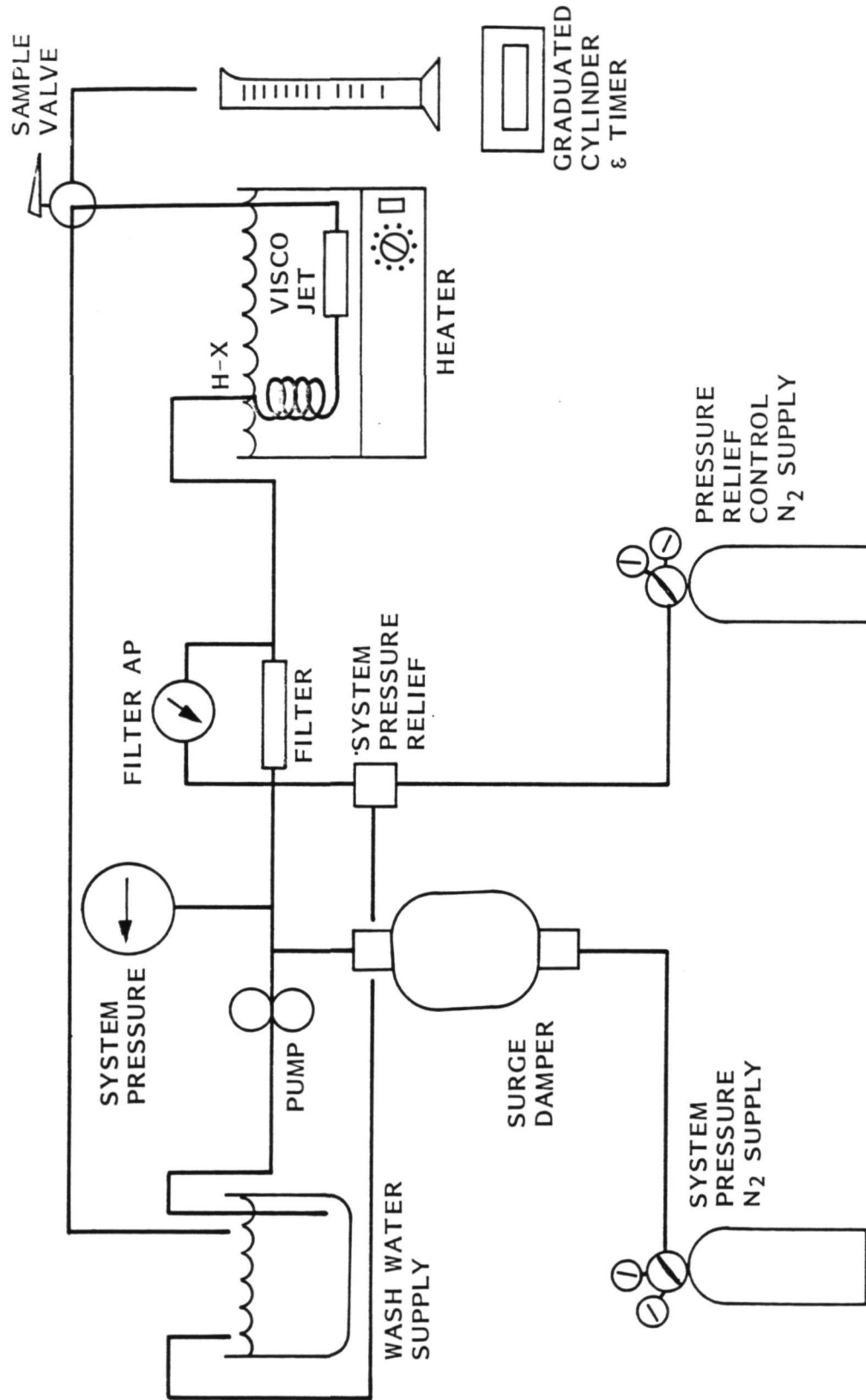


FIGURE 3-14 HYPERFILTRATION MODULE PRESSURE CONTROL TEST SCHEMATIC

The test rig consisted of a piston-type metering pump, a surge damper, a pre-filter, a heated water bath, provision for flow rate measurement, pressure gages, and a relief valve. The heated bath was used to heat the viscojet and fluid entering the viscojet, since it was not practical to heat the whole system.

The working fluid was the brine obtained for concentration of the wash water collected at LMSC. The water was concentrated by utilizing a commercial R.O. module.

In operation, the pump stroke was adjusted to provide a constant flow through the viscojet at a known pressure. The relief valve was then set higher than this pressure and did not ordinarily crack. Periodically, the water flow from the viscojet was collected and the flow rate was measured.

Viscojet testing was conducted over an extended period (320 hours) with only a slight (1.2%) drop in performance. With a 250 micron nominal filter installed, no dirt accumulated in the filter but some accumulated on the inlet side of the viscojet. It was analyzed and consisted mostly of fine organisms (see feed filter development section).

Figure 3-15 presents the viscojet flow rate versus pressure data. The lines for 169°F and 74°F are almost parallel. The expression for flow rate versus pressure was obtained from a least squares curve fit.

Figure 3-16 presents the flow rate versus temperature data. Since the data were taken during a warm up transient, a small amount of temperature lag was incurred. The dotted line presents the estimated corrected curve based on a 75°F steady state point. The equation is based on a least squares curve fit.

Figure 3-17 presents the flow rate versus time data. Initial and final clear water points were run for reference purposes. The dotted line shows the slight degradation of clear water flow with time. This was evidently due to the accumulation of dirt from the wash water.

All runs were with wash water brine concentrated in a commercial R.O. module. Since the same wash water was continuously recirculated, evaporation slowly reduced the overall quantity of water. Weekly, the water quantity was returned to normal using distilled water. Variations in the wash water flow appeared to correspond to these additions, and are evidently due to a slight thickening of the solution as the water evaporated. The wash water data also exhibited the same slight rate change with time that the clear water did.

### 3.16 Feed Filter

A shower water collection was made and a feed filter test was run. Both 250 micron nominal (350 absolute) and 70 micron nominal (105 absolute) filters were tested. One of the filters is shown in Figure 3-18.

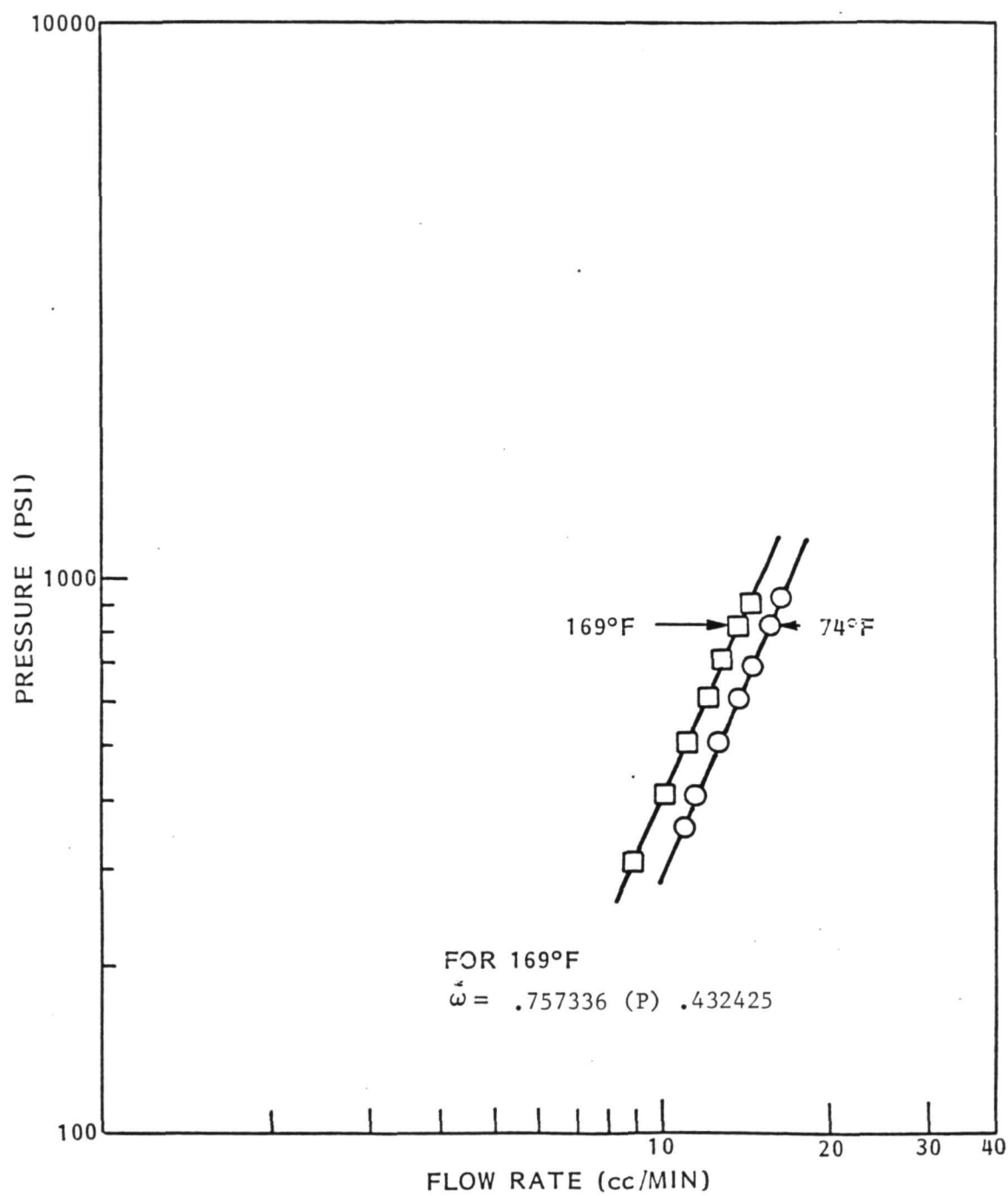


FIGURE 3-15

VISCO JET FLOW RATE VS PRESSURE

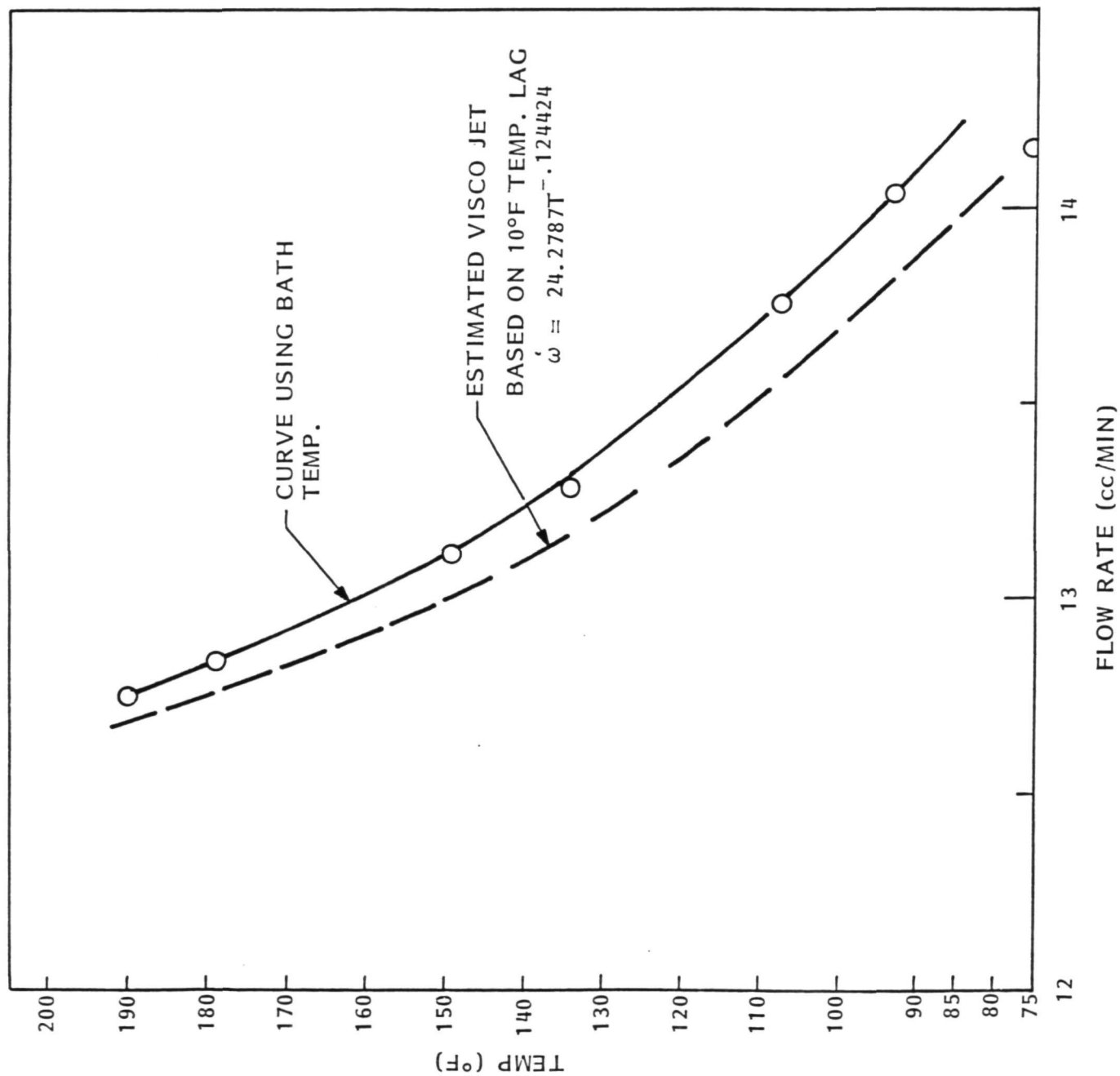


FIGURE 3-16  
VISCO JET FLOW RATE VS TEMPERATURE

DATA NORMALIZED  
WITH EQ.

$$\omega_2 = \omega_1 \left( \frac{168}{T} \right)^{-.12442} * \left( \frac{650}{P} \right)^{.432425}$$

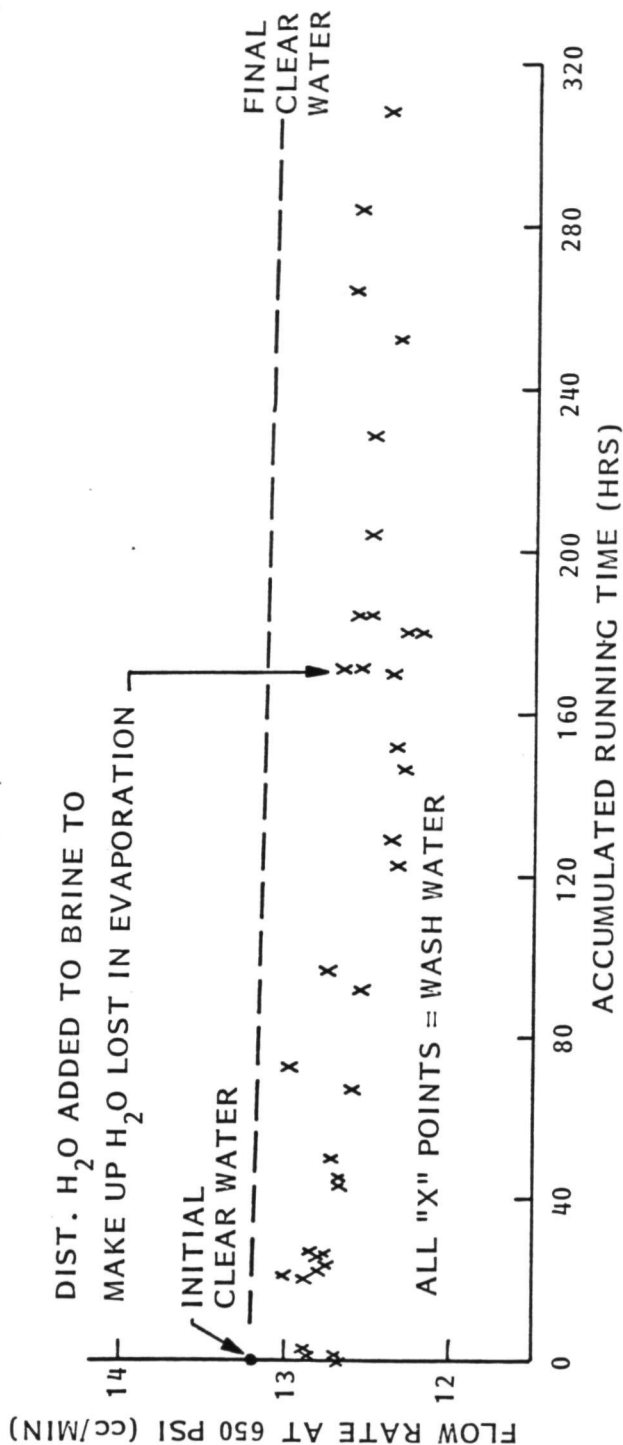


FIGURE 3-17

VISCO JET FLOW RATE VS TIME

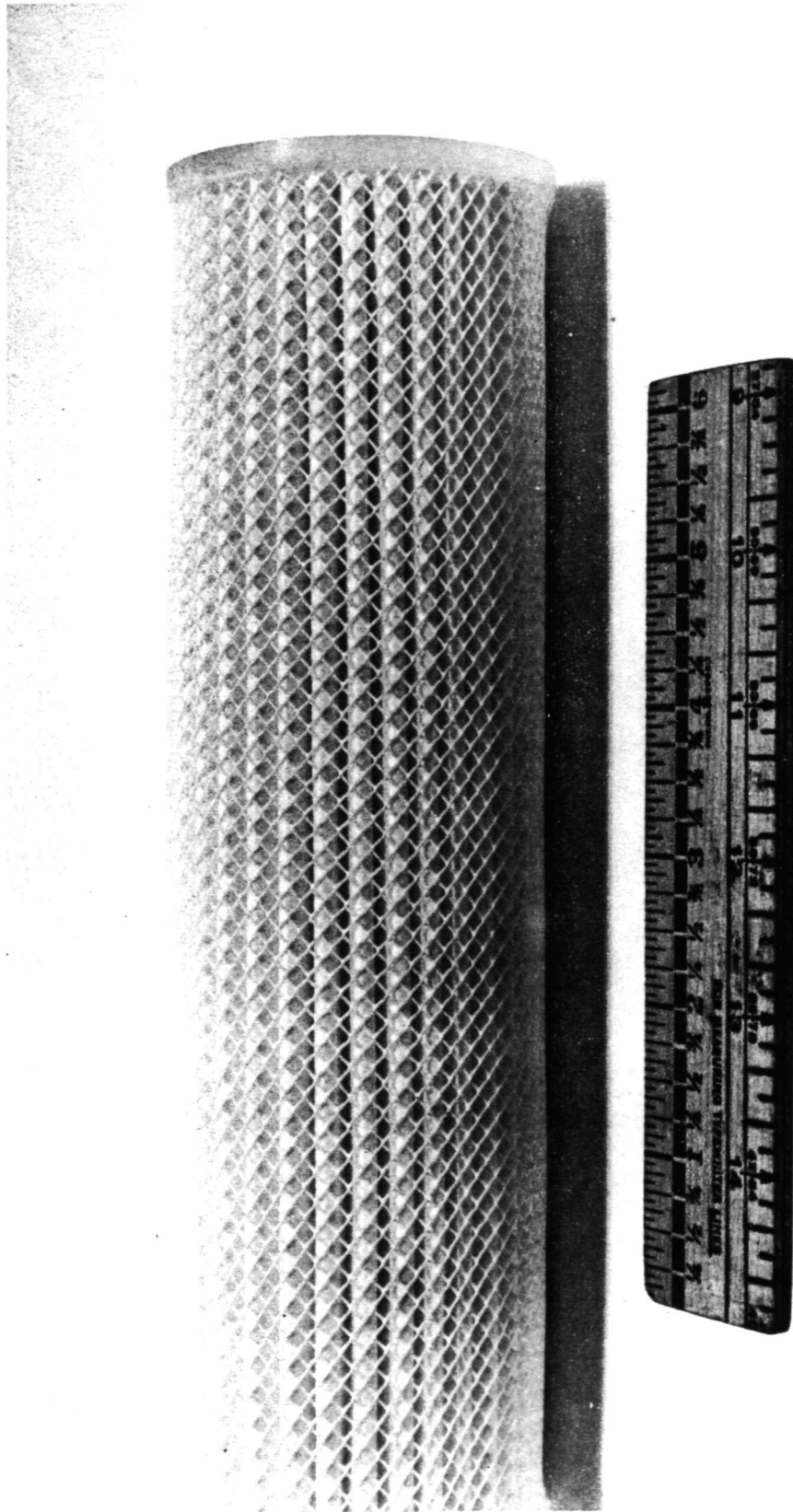


FIGURE 3-18 FEED FILTER

Figure 3-19 shows the pressure drop versus accumulated flow through three filters, and the line represents the maximum pressure drop. The pressure drop for run 1 was lower than that of run 2 and the 70 micron test, as less dirt accumulated (.085 gms for run 1 vs .116 gms for run 2). This was possibly due to statistical variations in the wash water samples. Dirt accumulation for the 70 micron test was about the same as for run 2.

The material which accumulated was mostly lint, mixed with a small amount of hair. The lint evidently came from the cotton clothes and towels.

Figure 3-20 shows the pressure drop versus flow characteristics of both clean and dirty filters. The curve for the dirty filter has been extrapolated in the most conservative fashion.

Based on the data of Figure 1 and 2, operation of the system for 180 days with a daily process volume of 27 gal and a process rate of .05 GPM requires 370 square inches of filter area. Both primary and backup filters used on the preprototype system will therefore have at least 370 square inches of area.

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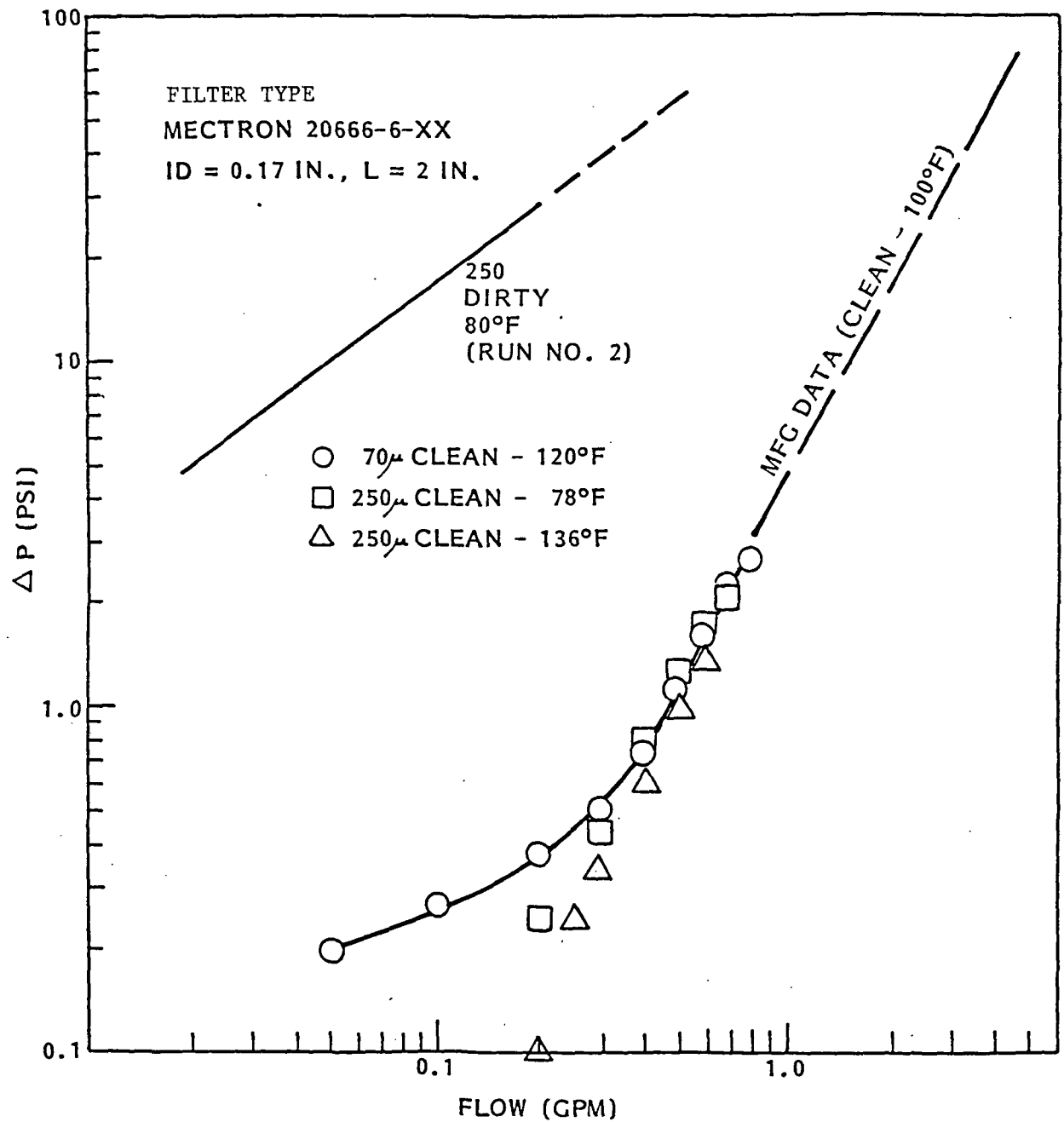


FIGURE 3-20.

HYPERFILTRATION FILTER PRESSURE DROP VS FLOW RATE

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## SECTION 4

SYSTEM LEVEL TESTING

System level testing was initiated at LMSC in August 1980 after the module had been received from ABCOR and integrated into the Hyperfiltration Washwater Reclamation System. The system level testing consisted of calibration of (1) flow meters, (2) metering pumps, (3) pressure transducers and (4) pressure switches and regulators followed by checkout with cold water then hot water and final testing with synthetic washwater. This section describes the results of these activities.

## 4.1 SYSTEM CALIBRATION

The visco-jets that control brine flow were calibrated over a range of 800 to 1000 psi which was the expected module operating pressure. The results of this calibration are presented below:

<u>VISCO-JET UPSTREAM PRESSURE</u> psi	<u>VISCO-JET LIQUID FLOW RATE</u> cc/min
1000	20
900	19
800	18

The permeate outlet flow meter was calibrated over a range of approximately 20 to 200 cc/min. The results of this calibration are presented below.

<u>PERMEATE FLOW RATE</u> cc/min	<u>FLOW METER</u> <u>OUTPUT VOLTAGE</u> <u>VOTES</u>
194	5.0
169	4.5
129	3.5
97	2.5
58	1.5
24	0.5

The brine outlet flow meter was calibrated over a range of approximately 10 to 20 cc/min. The results of this calibration are presented below:

<u>BRINE FLOW RATE</u> cc/min	<u>FLOW METER</u> <u>OUTPUT VOLTAGE</u> <u>VOLTS</u>
22	3.6
19	3.0
16	2.1
12	1.0

Difficulties were encountered with the brine flow meter subsequent to this calibration and the unit was returned to the vendor (Flow Technology, Phoenix, Arizona) for repair. When the unit is returned a new calibration will have to be established. The feed pump outlet pressure transducer was calibrated over a range of 150 to 1300 psi. The results of this calibration are presented below:

<u>PRESSURE</u> <u>psi</u>	<u>TRANSDUCER OUTPUT</u> <u>VOLTAGE</u> <u>VOLTS</u>
1300	5.0
1050	4.0
800	3.0
550	2.0
275	1.0
150	0.5

The feed pump accumulator was charged to 425 psi with nitrogen and the pump stroke was adjusted to obtain a total flow rate of 0.05 gpm. The NaOCl pump stroke was adjusted to its minimum output which resulted in a flow rate of 0.58 cc/min. This is approximately three times the stoichiometric flow rate which is higher than originally planned but is judged to be acceptable. The originally planned NaOCl flow rate was 0.4 cc/min which is twice the stoichiometric flow rate.

Data were taken during the system level test to allow an approximate calibration of the feed and permeate conductivity detectors. The results of this test are as follows:

<u>CONDUCTIVITY</u> <u>(<math>\mu</math> MHOS/CM)</u>	<u>METER OUTPUT</u> <u>VOLTAGE</u>
1000	0.5
0	0

The final step in the system level calibration was adjusting and setting pressure switches, regulators and relief valves. The final setting of these devices is presented in Table 4-1.

#### 4.2 CHECKOUT

A complete system checkout was conducted with room temperature distilled water prior to insulating the system. The system was operated for about 6 hours in this mode. System pressures and flow rates were checked periodically. The permeate flow rate was 197 cc/min and the brine flow rate was 17 cc/min which were the expected values. The module pressure reached an upper value of 600 psi early in the testing but quickly dropped to 525 to 500 psi where it remained for the balance of the room temperature water testing.

TABLE 4-1

FINAL PRESSURE SWITCH, RELIEF VALVEAND REGULATOR SETTINGS

<u>COMPONENT</u>	<u>ITEM NO.</u>	<u>SET POINT</u>
TANK REFILL SYSTEM ENABLE	2G	8 psi
FEED PUMP LOW PRESSURE SHUT-DOWN	2A	1 psi
TANK LOW LEVEL SHUT-DOWN	2B	5 psi
TANK HIGH LEVEL WARNING	2D	11.5 psi
NaOCl TANK LOW LEVEL SHUT-DOWN	2E	5 psi
FEED TANK GAS PRESSURE RELIEF	6B	10 psi
FEED TANK LIQUID PRESSURE RELIEF	6A	20 psi
FILTER DIFFERENTIAL PRESSURE SHUT-DOWN	1B	8 psi
PERMEATE OUTLET BACK PRESSURE RELIEF	8C	10 psi
MODULE BRINE HIGH PRESSURE RELIEF	7	1250 psi
MODULE PERMEATE LOW PRESSURE RELIEF VALVES	6C, 8A	30 psi
BRINE OUTLET LOW PRESSURE RELIEF VALVE	8B	30 psi
NaOCl TANK LIQUID RELIEF	44	30 psi
NaOCl TANK GAS RELIEF	6D	12 psi

All elements of the system operated successfully with the exception of the brine outlet flow meter. As indicated previously difficulties were experienced with this unit and it was returned to the vendor for repair. When the repair is complete the unit will be shipped to NASA. The flow meter was bypassed and testing was continued. After the room temperature water testing was completed thermal insulation was placed on the unit.

The next checkout run was conducted with hot distilled water and with the system heaters operating. All aspects of the system appeared to function normally with hot water, however, the module operating pressure dropped to about 350 psi. The feed pump flow rate was checked and found to be at the correct value. The reduced module pressure was attributed to the effects of the increased (160°F) operating temperature. ABCOR data indicates that flux increases considerably with increased temperature for a given pressure which confirms this conclusion.

#### 4.3 TESTING WITH SYNTHETIC WASHWATER

System level testing with synthetic washwater was initiated on 28 August 1981 and was carried out for two days. During that time the system was operated for approximately 14 hours and 42 gallons of synthetic washwater was processed. Approximately 50 gallons of synthetic washwater was prepared per the formulation presented in Table 4-2. The synthetic washwater was loaded into a commercial hot water heater and tank where it was maintained at approximately 160°F. This simulated the Spacecraft interface that the system was designed to meet. The synthetic washwater was then transferred into a 5 gallon tank that could be pressurized. The 5 gallon tank was utilized to load the hyperfiltration system feed tank. This process was repeated about once per hour during the synthetic washwater testing to insure that the feed tank would not empty. The system operated normally throughout the two-day period and water samples and system data were taken hourly. During the first day of testing, operation of the various system shutdowns and warnings was verified. The system operating performance is presented in Table 4-3 and consists of feed tank temperature, module temperature, module pressure, brine flow rate, permeate flow rate and % conversion. The chemical analysis data of the feed, permeate and brine solutions is presented in Table 4-4 along with the observed and calculated intrinsic rejections. The intrinsic rejection was calculated using the following formulas:

$$R_I = 1 - \frac{\log (1-Y [1-R_o])}{\log (1-Y)}$$

Where:  $R_I$  = Intrinsic Rejection

$R_o$  = Observed Rejection

$Y$  = Conversion

Conversion =  $\frac{\text{Module permeate flow rate}}{\text{Inlet Feed Flow Rate}}$

TABLE 4-2

FORMULATION FOR SYNTHETIC WASHWATERUSED IN SYSTEM LEVEL TEST

REAGENT	REAGENT STATE	AMOUNT ADDED PER 50 GALS
AMMONIUM HYDROXIDE	29% AQ. SOLUTION	17.60 cc
DEXTROSE	ANHYDROUS POWDER	1.514 g
LACTIC ACID	85% AQ. SOLUTION	28.766 g
POTASSIUM HYDROXIDE	PELLETS (CONTAIN 10-15% WATER)	8.895 g
SODIUM CHLORIDE	CRYSTAL	34.633 g
SODIUM LAURYL SULFATE	POWDER	69.644 g
UREA	CRYSTAL	12.112 g

TABLE 4-3  
SYSTEM OPERATING PARAMETERS DURING SYNTHETIC WASHWATER TEST

DATE	TIME	FEED TEMP OF	MODULE TEMP OF	PERMEATE OUT TEMP OF	MODULE PRESSURE psi	BRINE FLOW RATE cc/min	PERMEATE FLOW RATE cc/min	% CONVERSION OP/OF
8/28	1000	142	168	173	280	5.13	234.4	97.9
	1100	158	162	160	325	10.3	217.4	95.9
	1200	160	161	159	325	12.2	202.7	94.3
	1300	152	160	157	350	12.8	204.1	94.1
	1400	145	155	154	375	13.9	204.1	93.6
	1500	156	156	155	370	13.0	204.1	94.0
	1600	158	158	158	370	12.8	204.1	94.1
	0900	168	182	180	275	11.5	217.4	95.0
8/29	1000	162	164	163	350	13.3	200.0	93.8
	1100	162	162	162	360	13.3	200.0	93.8
	1200	162	162	162	370	13.7	200.0	93.6
	1300	159	162	162	380	14.9	217	93.6
	1400	162	162	162	390	14.3	203	93.4
	1500	165	163	163	390	15.9	197	92.5

TABLE 4-4  
CHEMICAL ANALYSIS DATA - SYNTHETIC WASHWATER TEST

DATE	TIME	CONDUCTIVITY					UREA				
		CONCENTRATION $\mu\text{MHOS/CM}$			REJECTION %		CONCENTRATION MG/L			REJECTION %	
		FEED	CONC	PERM	OBSERVED	INTRINSIC	FEED	CONC	PERM	OBSERVED	INTRINSIC
8/28	1000	582	2410	900	-	-	70	77	4	94.3	98.5
	1100	595	2570	1180	-	-	70	85	2	97.1	99.1
	1200	595	2400	1550	-	-	70	100	26	62.6	84.8
	1300	595	2460	1220	-	-	70	136	4	94.3	98.0
	1400	627	2600	1500	-	-	60	172	26	56.7	81.0
	1500	627	2460	1420	-	-	60	162	15	75.0	90.5
	1600	627	2700	1360	-	-	60	83	-	-	-
8/29	0900	620	2180	900	-	-	66	55	-	-	-
	1000	620	2200	570	8.1	28.9	66	51	43	34.8	66.1
	1100	620	2400	570	8.1	28.9	66	72	32	51.5	78.2
	1200	595	2350	600	-	-	60	68	23	61.7	83.8
	1300	595	2350	1200	-	-	60	64	28	53.3	79.0
	1400	595	2330	1070	-	-	60	68	28	53.3	78.9
	1500	595	2280	870	-	-	60	66	45	25.0	54.1



TABLE 4-4 (cont'd) CHEMICAL ANALYSIS DATA - SYNTHETIC WASHWATER TEST

DATE	TIME	T.O.C					TOTAL RESIDUE				
		CONCENTRATION MG/L		REJECTION %		INTRINSIC	CONCENTRATION MS/L		REJECTION %		
		FEED	CONC	PERM	OBSERVED		FEED	CONC	PERM	OBSERVED	INTRINSIC
8/28	1000	125	1230	35	72.0	91.7	1016	3892	540	46.9	81.0
	1100	125	1435	21	83.2	94.5	1016	5136	1216	-	-
	1200	205	1610	28	86.3	95.2	1004	4848	1436	-	-
	1300	205	1760	29	85.9	95.0	1004	5072	1436	-	-
	1400	205	2400	22	89.3	96.1	1104	5824	1332	-	-
	1500	255	1870	48	81.2	93.1	1104	6196	1248	-	-
	1600	255	2250	47	81.6	93.3	1104	5484	1160	-	-
8/29	0900	233	1000	51	78.1	92.2	1112	3076	1040	6.5	26.8
	1000	233	1050	37	84.1	94.2	1112	3452	716	35.6	66.7
	1100	233	947	28	88.0	95.7	1112	3656	748	32.7	63.7
	1200	233	1175	38	83.7	94.0	1100	3868	668	39.3	69.3
	1300	255	1260	41	83.9	94.0	1100	4068	1152	-	-
	1400	255	1300	52	79.6	92.2	1100	4160	952	13.5	39.3
	1500	255	1345	40	84.3	93.2	1100	3928	792	28.0	57.4

TABLE 4-4 (cont'd)

## CHEMICAL ANALYSIS DATA - SYNTHETIC WASHWATER

AMMONIA											
DATE	TIME	CONCENTRATION MG/L			REJECTION %		PH				
		FEED	CONC	PERM	OBSERVED	INTRINSIC	FEED	CONC	PERM		
8/28	1000	13	73	0.5	96.1	99.0	6.92	6.13	5.62		
	1100	13	50	8	38.5	72.2	6.92	6.02	6.40		
	1200	13	34	3	76.9	91.4	8.44	5.84	5.85		
	1300	13	25	11	15.4	43.9	8.44	5.74	6.58		
	1400	10	39	3	70.0	87.9	8.24	6.51	6.85		
	1500	10	33	8	20.0	50.4	8.24	6.40	6.13		
	1600	10	59	3	70.0	88.3	8.24	7.15	6.97		
8/29	0900	34	70	27	20.6	53.1	8.37	7.23	6.56		
	1000	34	67	34	0	0	8.37	6.76	7.03		
	1100	34	67	22	35.3	66.5	8.37	6.71	6.59		
	1200	34	62	28	17.6	46.2	8.72	6.78	7.05		
	1300	34	64	25	26.5	57.5	8.72	6.60	7.35		
	1400	34	140	14	58.8	82.9	8.72	6.58	7.35		
	1500	34	145	8	76.5	90.5	8.72	6.83	7.36		

A comparison of the chemical rejections obtained in the ABCOR synthetic wash-water test and the LMSC synthetic washwater test is presented in Table 4-5. The results indicate that in the tests at LMSC slightly higher rejections were obtained for ammonia, urea and total organic carbon while lower rejections were obtained for total residue and conductivity. Referring to the data in Table 4-4 the permeate conductivity was in many cases higher than the feed. This was also the case for a few of the total residue samples. One explanation for this might be that there was residual inorganic contamination either in the module on the permeate side or in the plumbing downstream of the module and that the test was not of sufficient duration to purge this residual contamination from the system.

Even though the rejections experienced at LMSC were higher than those experienced at ABCOR they were still below an acceptable value for a washwater reclamation system.

TABLE 4-5

COMPARISON OF ABCOR AND LMSC FINAL RESULTS

	ABCOR RESULTS		LMSC RESULTS <sup>(1)</sup>	
	% REJECTION		% REJECTION	
	OBS	INT	OBS	INT
AMMONIA	35.3	63.6	53.9	77.0
UREA	28.2	56.6	43.9	70.7
TOTAL ORGANIC CARBON	71.1 <sup>(2)</sup>	87.5 <sup>(2)</sup>	82.6	93.1
TOTAL RESIDUE	45.2	71.8	26.9	55.3
CONDUCTIVITY	0.8	3.4	0	0

(1) LMSC RESULTS ARE THE AVERAGE OF THE LAST 3 SAMPLES

(2) REPRESENT INITIAL NOT FINAL RESULTS

## SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

A number of problems remain to be solved before ZrO-PAA membrane technology can be successfully applied to processing of Spacecraft wastewater under realistic conditions. The problems are inherent in both (1) the transition from small to large surface-area ZrO-PAA modules, and (2) the nature of the ZrO-PAA membrane itself.

During this program excellent intrinsic hyperfiltration performance was achieved for ZrO-PAA membrane formed on single stainless steel tubes with carbon-black filteraid. However, intrinsic rejections obtained for a multi-tube module were consistently less than the single-tube rejections, falling below the 88% minimum believed necessary for wastewater processing. Therefore future efforts must focus on improving multi-tube module rejection capability to an acceptable level. This may require modification of membrane formation procedure and/or improved module hardware design.

Considerable data were generated during the program which indicate that ZrO-PAA membranes are susceptible to damage from mechanical shock and/or extended storage. Instability was shown to an equal degree for membranes formed with and without carbon-black filteraid. Clearly, this problem must be eliminated if the membrane is to be used in a life-support function such as in processing of Spacecraft wastewater. Future work should be concentrated on improving the inherent stability of the ZrO-PAA membrane through modified formation technique. If this is not possible, means will have to be devised to protect the membrane from shock damage and/or to automatically repair damage through in-situ membrane regeneration.

In tests with sodium nitrate and synthetic wastewater feeds, the rejection of the ZrO-PAA module was found to be extremely sensitive to concentration polarization effects resulting from low-velocity, high-conversion operation. These effects, combined with the low intrinsic module membrane rejection ( $\sim 75\%$ ), resulted in unacceptable rejections of various key wastewater constituents. The results emphasize the need to obtain higher intrinsic module rejection. Once acceptable intrinsic rejection is obtained, the ability of a ZrO-PAA module to successfully process wastewater under low-velocity, high-conversion conditions must still be demonstrated.

Even though slightly higher intrinsic rejections were experienced during the system level synthetic wastewater test at LMSC the rejections were still less than that required for a wastewater reclamation system.

The supporting system elements did operate satisfactorily and provide a test bed suitable for the evaluation of future membrane modules.

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## APPENDIX A

### ZrO-PAA MEMBRANE FORMATION METHODOLOGY

#### HYPERFILTRATION SYSTEM

##### System Design

Basic system design as it pertains to ZrO-PAA membrane formation technique has been discussed in detail elsewhere (e.g. this report, Ref. 20, Ref. 23). These discussions emphasize the need for 1) minimization of stagnant area and 2) use of pH-, temperature-, and pressure-resistant materials.

Avoidance of stagnant space permits rapid change-over of solutions (e.g. during pH adjustment), allows efficient cleaning, and prevents accumulation of contaminants which could subsequently interfere with the membrane formation process. However the presence of some dead space is unavoidable, as in the case of "tees" used to connect pressure gauges, sample valves, etc. These items should be connected with swaged (versus threaded) fittings to allow easy periodic disassembly and cleaning.

To allow complete drainage of the system each horizontal run should be slightly pitched. A valve should be located at the highest point in the system to permit adequate venting.

All system materials should be able to withstand the following conditions:

1 M NaOH at 50°C (periodic)

1 M HNO<sub>3</sub> at 50°C (periodic)

85°C at pH 5-8 (continuous)

Materials used in this program were restricted to 304 stainless steel, 316 stainless steel, polyethylene, polypropylene, viton rubber, butyl rubber, and Teflon.

In addition to being pH- and temperature- resistant, the high-pressure components of the system must be able to withstand continuous operating pressures of up to 70 kg/cm<sup>2</sup>. For precautionary purposes these components should therefore be rated for 100 kg/cm<sup>2</sup> or greater.



## Component Selection

In general, specific brands of individual system components need not be recommended. The components must only be mechanically reliable and resistant to the extremes listed above. However, several key items -- the high-pressure feed pump, accumulator (pulsation dampener), and prefilter -- require further mention.

Either diaphragm, plunger, or centrifugal pumps may be used for ZrO-PAA membrane formation. The pump must have the proper flow capacity and output pressure, and all wetted materials must be suitably pH- and temperature-resistant. The last requirement applies in particular to the choice of diaphragm or packing material used. Pumps successfully used in this program were as follows:

- 1) Yarway Cyclophram Metering Pump  
Model 0721-26-52-31  
Yarway Corporation  
Blue Bell, Pa.

max. pressure output	140 kg/cm <sup>2</sup>
max. flow output	3.3 lpm
diaphragm material	Teflon
other wetted parts	316 SS

- 2) Gaulin Triplex Plunger Pump  
Model 300 CGD  
Gaulin Corporation  
Everett, Mass.

max. pressure output	210 kg/cm <sup>2</sup>
max. flow output	12 lpm
packing material	Teflon/asbestos
other wetted parts	304 SS

Despite an extensive search, no commercially-available accumulator could be found which had both the necessary chemical resistance and a sufficient dampening range. Therefore a system meeting both these requirements was fabricated in-house (see Figure A-1). The accumulator consists of a bladderless 304 stainless steel sampling cylinder\* (volume 2250 cc, pressure rating 127 kg/cm<sup>2</sup>) pre-charged with high-purity nitrogen. To operate the system, the ball valve separating the accumulator from the circulation loop is closed and the accumulator is charged with nitrogen to 17-21 kg/cm<sup>2</sup>. A needle valve is then closed to isolate the accumulator from the nitrogen cylinder. After starting the feed pump, pressure in the circulation loop is increased to just over that in the accumulator, and

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\*Part no. 8HD2250, Hoke Inc., Cresskill, N.J.

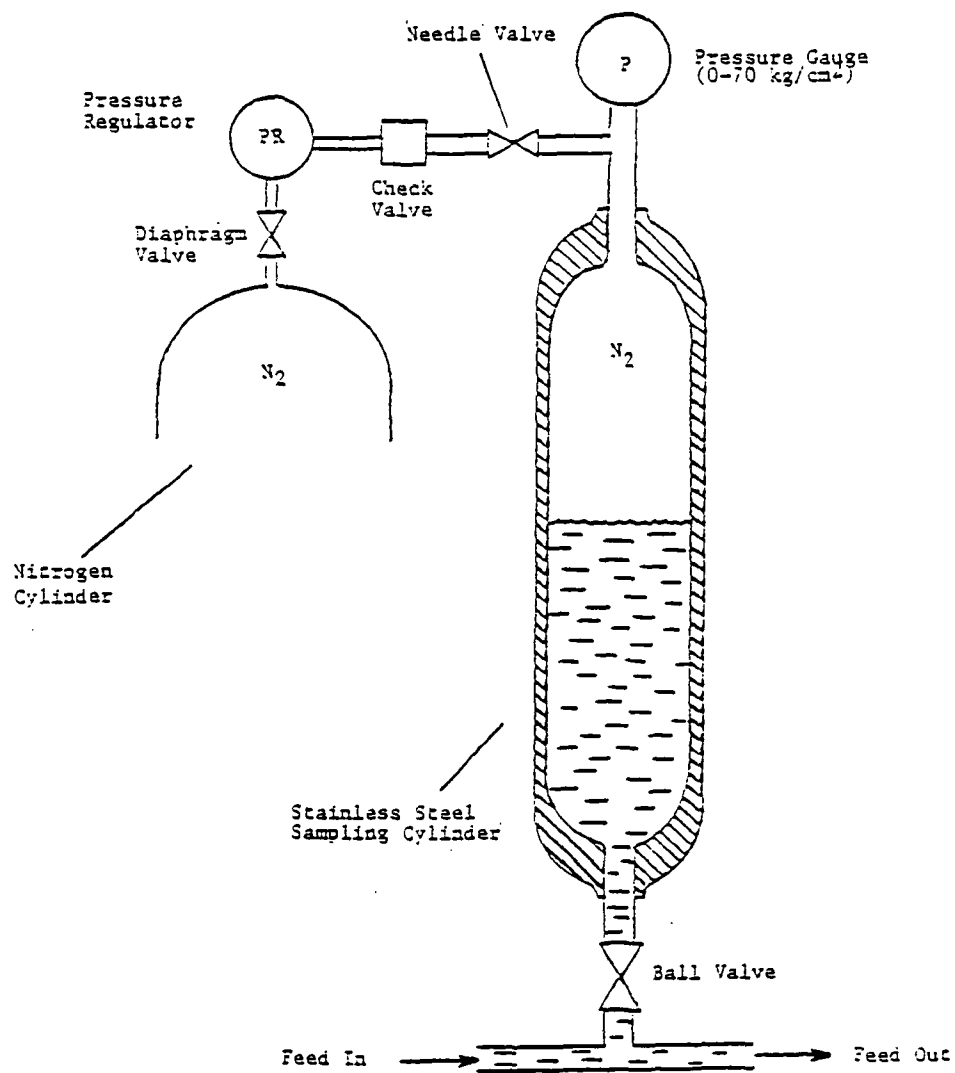


Figure A-1. Bladderless Accumulator System

the ball valve is opened to the system. Feed solution then enters the accumulator, which prevents escape of nitrogen into the circulation loop. The resultant nitrogen cushion provides adequate pulsation dampening over the pressure range of interest (21-84 kg/cm<sup>2</sup>).

To prevent deposition of contaminants on the porous supports it is recommended that the feed solution be prefiltered during membrane formation, membrane stripping, and salt and washwater processing. During this program a stainless steel strainer\* with pore-size ratings of 140 or 230 microns was used in membrane formation experiments, while a somewhat more open strainer (440 microns) was used in washwater processing. During membrane evaluations with standard salt solutions a relatively tight (25-micron) depth-type filter\*\* was used. The filter elements were made from borosilicate glass bonded with epoxy resin. 25-micron depth filters were also used in the membrane stripping experiments, but in this case elements formed with a special tetrafluoroethylene binder were chosen because of the severe pH extremes.

#### CHEMICAL SELECTION

The various chemicals recommended for formation and stripping of ZrO-PAA membranes are described below. In addition to quality, the minimum quantity required for up to 20 membrane formation/stripping cycles is indicated.\*\*\* Specific manufacturers are listed only as required.

##### Carbon Black

Regal SR or Sterling R (mean particle size 75 mμ)  
Cabot Corporation  
Special Blacks Division  
Boston, Mass.

quality: standard  
quantity: 3.8 liters (minimum order)

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\* Part no. SS-6TF, Nupro Company, Willoughby, Ohio.

\*\* Part no. 95 S, Balston Inc., Lexington, Mass.

\*\*\* Based on a 100-liter feed volume except for the HNO<sub>3</sub>, NaOH, and oxalic acid quantities, which are based on a 20-liter feed volume.

### Zirconyl or Zirconium Nitrate

- 1) zirconyl nitrate (zirconium dinitrate oxide)  
 $\text{ZrO}(\text{NO}_3)_2 \cdot n \text{H}_2\text{O}$   
Ventron Corporation  
Alfa Products Division  
Danvers, Mass.

quality: standard  
quantity: 500 g

- or 2) zirconium nitrate  
 $\text{Zr}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$   
Atomergic Chemetals  
Plainview, N.Y.

quality: 99.5%  
quantity: 500 g

### Polyacrylic Acid

Acrysol A-3, 25% w/w aqueous PAA solution  
Rohm & Haas Tennessee, Inc.  
Knoxville, Tenn.

quality: standard  
quantity: 18 kg (minimum order)

### Sodium Nitrate

$\text{NaNO}_3$ , crystal

quality: reagent grade  
quantity: 9 kg

### Sodium Hydroxide

$\text{NaOH}$ , flakes or pellets

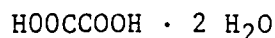
quality: technical grade  
quantity: 80 kg

### Nitric Acid

$\text{HNO}_3$ , 69.0-71.0%

quality: reagent grade  
quantity: 36 kg

### Oxalic Acid Dihydrate



quality: technical grade

quantity: 500 g

### MEMBRANE FORMATION PROCEDURES

The various steps of the ZrO-PAA membrane formation process are described in detail below. Each of the feed solutions mentioned should be prepared with high-purity water (distilled, deionized, or RO-treated).

#### System Cleaning

1. Prepare 20-l volume of 1 M NaOH. Circulate through system (excluding supports) for 1 hour at 30-50°C, 14-28 kg/cm<sup>2</sup>. Drain and rinse.
2. Prepare 20-l volume of 1 M HNO<sub>3</sub>. Circulate through system (excluding supports) for 1 hour at 30-50°C, 14-28 kg/cm<sup>2</sup>. Fresh stainless steel supports may be inserted for final 30 minutes of acid cleaning in order to remove possible corrosion products. (Fresh ceramic supports do not require cleaning.) Drain and rinse.
3. Repeat base and acid washes if necessary.

Note: All stagnant areas must be flushed thoroughly at the end of each cleaning step.

#### Filteraid Application\*

1. Prepare 30-100 liters of 25-50 ppm carbon black (Cabot Regal SR or Sterling R) in water. Dispersion may be aided by pre-mixing required amount of carbon in 1 liter of water using high-speed blender.
2. Circulate carbon suspension over porous supports for 30 minutes at 25-30°C, 28-42 kg/cm<sup>2</sup>, 4-9 mps average feed velocity. The suspension may be visually depleted in less than 30 minutes if a large support surface-area is being used, in which case additional doses (~10-20 ppm) of carbon may be added.

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\* Only for supports having an average pore size rating of more than 1 micron.

### ZrO Application

1. Prepare 30-100 liters of 0.05 M  $\text{NaNO}_3$  and  $1 \times 10^{-4}$  M ( $\sim 40$  ppm)  $\text{ZrO}(\text{NO}_3)_2$  or  $\text{Zr}(\text{NO}_3)_4$ . Adjust pH to  $4.0 \pm 0.2$  using  $\text{HNO}_3$ .
2. Circulate solution past porous supports at 25-30°C and 4-9 mps average feed velocity, raising pressure to 70 kg/cm<sup>2</sup> as soon as possible.
3. ZrO membrane is considered formed when flux decreases to 200-500 l/m<sup>2</sup>-hr and/or when conductivity rejection increases to 30-50%. If these performance levels are not reached within 1-2 hours, additional doses ( $\sim 20$ -40 ppm) of zirconium may be added.

### PAA Application

1. Adjust pH to  $2.0 \pm 0.1$  with  $\text{HNO}_3$  and add 50 ppm PAA (200 ppm Acrysol A-3).
2. Add NaOH to raise pH in stepwise manner (2 to 3, 3 to 4, etc.) to pH  $7.0 \pm 0.2$ , waiting 30 minutes at each intermediate level.
3. If membrane performance is unsatisfactory, return pH to 2.0 and repeat pH excursion using an additional 0-50 ppm PAA.

### MEMBRANE REGENERATION PROCEDURES

Any of a number of techniques may be used to recover rejection lost due to shutdown or extended storage. These include the following:

- Repetition of pH excursion from 2.0 to 7.0 without additional PAA.
- Repetition of pH excursion from 2.0 to 7.0 with additional 25-200 ppm PAA.
- Repetition of pH excursion from 2.0 to 7.0 with additional 20-40 ppm  $\text{ZrO}(\text{NO}_3)_2$  or  $\text{Zr}(\text{NO}_3)_4$  plus 25-200 ppm PAA.
- Repetition of entire ZrO-PAA membrane formation sequence, with or without carbon-black filteraid.

## MEMBRANE REMOVAL PROCEDURES

The stainless steel supports may be prepared for re-use through the membrane removal techniques discussed previously in this report (see Section 4).

## MEMBRANE STORAGE

ZrO-PAA membranes should be stored completely immersed in water at all times.

APPENDIX B

DETAILED HYPERFILTRATION PERFORMANCE DATA  
FOR ZrO-PAA MEMBRANES FORMED ON  
SINGLE-TUBE SUPPORTS



TABLE B-1. DETAILED HYPERFILTRATION PERFORMANCE DATA FOR ZrO-PAA MEMBRANES FORMED WITHOUT CARBON-BLACK FILTERAID (0.05 M NaNO<sub>3</sub>, 30°C, 4.6 MPS)

Membrane Formation No.	Operating Pressure (kg/cm <sup>2</sup> )	Porous Support	ZrO		ZrO-PAA		Regenerated ZrO-PAA	
			Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)
01	67	SS 0.5μ 01	244	44.6	86.6	84.3	64.0	92.0
		SS 0.5μ 02	270	45.7	62.5	84.1	48.6	92.2
		ceramic 0.3μ 01	219	43.5	59.8	76.4	62.1	79.8
		ceramic 0.3μ 02	--	--	--	--	53.8	84.2
02	60	SS 0.5μ 01	482	27.1	36.3	89.1	--	--
		SS 0.5μ 02	703	25.0	46.3	91.9	--	--
		ceramic 0.3μ 03	413	31.3	36.3	86.1	--	--
		ceramic 0.3μ 04	489	30.2	36.7	87.5	--	--
03	60	SS 0.5μ 01	224	18.5	78.6	45.0	45.5	74.5
		SS 0.5μ 02	202	33.3	63.7	61.7	31.9	84.8
		ceramic 0.3μ 05	229	46.3	52.8	66.7	25.8	68.4
		ceramic 0.3μ 06	229	44.4	51.3	70.0	27.7	63.8
04	60	SS 0.5μ 01	236	7.3	95.6	55.6	--	--
		SS 0.5μ 02	204	9.1	76.7	54.8	--	--
		ceramic 0.3μ 07	244	7.3	124	37.3	--	--
		ceramic 0.3μ 08	209	7.3	97.1	30.2	--	--

(continued)

TABLE B-1 (continued)

Membrane Formation No.	Operating Pressure (kg/cm <sup>2</sup> )	Porous Support	ZrO		ZrO-PAA		Regenerated ZrO-PAA	
			Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)
05	60	SS 0.5μ 01	202	8.3	67.4	43.1	--	--
		SS 0.5μ 02	135	12.5	42.4	65.5	--	--
		ceramic 0.3μ 09	229	6.3	133	22.4	--	--
		ceramic 0.3μ 10	216	14.6	96.3	31.1	--	--
06	60	SS 0.5μ 01	168	15.8	--	--	--	--
		SS 0.5μ 03	246	1.1	--	--	--	--
		ceramic 0.3μ 11	192	13.7	--	--	--	--
		ceramic 0.3μ 12	238	11.6	--	--	--	--
07	70	SS 0.5μ 01	319	21.7	65.4	57.7	--	--
		SS 0.5μ 03	280	34.8	58.4	67.9	--	--
		ceramic 0.3μ 13	140	59.8	35.5	74.8	--	--
		ceramic 0.3μ 14	--	--	28.5	75.2	--	--
08	70	SS 0.5μ 04	112	22.2	--	--	--	--
		SS 0.5μ HYP 01	78.6	33.3	--	--	--	--
09	70	SS 0.5μ 04	258	32.2	106	58.8	46.3	82.1
		SS 0.5μ HYP 01	190	34.4	76.2	61.9	32.3	81.3
		ceramic 0.3μ 15	375	25.6	124	66.6	67.7	83.2
10	70	SS 0.5μ 04	234	38.1	103	60.0	57.9	78.0
		SS 0.5μ HYP 01	168	40.5	59.3	62.6	33.3	81.2
		ceramic 0.3μ 16	229	45.2	87.8	68.6	54.7	83.7

(continued)

TABLE B-1 (continued)

Membrane Formation No.	Operating Pressure (kg/cm <sup>2</sup> )	Porous Support	ZrO		ZrO-PAA		Regenerated ZrO-PAA	
			Flux (1/m <sup>2</sup> -hr)	Ref (%)	Flux (1/m <sup>2</sup> -hr)	Ref (%)	Flux (1/m <sup>2</sup> -hr)	Ref (%)
11	70	SS 0.5μ 04	194	36.0	67.2	51.5	56.2	66.2
		SS 0.5μ HYP 01	126	31.4	49.9	47.5	39.6	64.9
		ceramic 0.3μ 17	285	22.1	94.9	72.1	86.6	84.5
12	70	SS 0.5μ 04	219	29.2	71.5	67.9	--	--
		SS 0.5μ HYP 01	119	32.3	59.8	50.0	--	--
		ceramic 0.3μ 18	323	37.5	67.6	77.7	--	--
13	70	SS 0.5μ 04	333	5.1	--	--	--	--
		SS 0.5μ HYP 02	272	7.7	--	--	--	--

TABLE B-2. DETAILED HYPERFILTRATION PERFORMANCE DATA  
FOR ZrO-PAA MEMBRANES FORMED WITH CARBON-BLACK  
FILTERAID (0.05 M NaNO<sub>3</sub>, 70 KG/CM<sup>2</sup>, 30°C, 4.6 MPS)

Membrane Formation No.	Porous Support	ZrO		ZrO-PAA	
		Flux (1/m <sup>2</sup> -hr)	Rej (%)	Flux (1/m <sup>2</sup> -hr)	Rej (%)
14	SS 0.5μ 04	440	41.5	94.2	92.6
	SS 0.5μ HYP 02	613	43.9	84.0	93.9
	ceramic 0.3μ 19	472	31.7	103	86.1
15	SS 0.5μ 04	390	35.4	83.4	90.3
	SS 0.5μ HYP 02	430	38.0	74.2	92.8
	ceramic 0.3μ 20	506	24.1	77.8	86.8
16	SS 0.5μ 04	355	33.8	56.2	91.0
	SS 0.5μ HYP 01	331	37.8	51.4	90.9
	SS 0.5μ HYP 02	334	35.7	52.0	90.7
	ceramic 0.3μ 21	336	32.4	55.5	85.2